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FINAL PROJECT REPORT

on

PILOT PLANT MOVING GRATE FURNACE STUDY OF LIMESTONE-DOLOMITE FOR CONTROL OF SULFUR OXIDE IN COMBUSTION FLUE GAS

CONTRACT PH-22-68-68

to

DIVISION OF PROCESS CONTROL ENGINEERING
NATIONAL AIR POLLUTION CONTROL
ADMINISTRATION

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by

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TABLE OF CONTENTS

	PAGE NO.
SUMMARY	1
CONCLUSIONS	3
RECOMMENDATIONS	5
ACKNOWLEDGMENT	6
INTRODUCTION	7
PILOT PLANT APPARATUS	7
System Velocities and Residence Time	11
Injector Design	14
Gas Sampling System	14
Wet Test Gas Analysis	16
Particulate Sample System	16
TEST MATERIALS AND PREPARATION	20
Injection Materials	20
Test Coals	25
EXPERIMENTAL RESULTS AND DISCUSSIONS	25
SO_2 Sampling Points	25
Effect of Additive Feed Rate	27
Effect of Particle Size	29
Effect of Injection Temperature	31
Effect of Injection Air Velocity	31
Coal-Limestone Mixtures	32
Sulfur Balance	34
Calcination Levels	35

TABLE OF CONTENTS CONT'D

	PAGE NO.
Calcium Oxide Utilization and Additive Efficiency	38
Red Mud Injections	40
APPENDIX	
A - Test Run Data	A-1
B - Coal Data	B-1
C - References	C-1
FIGURES	
1. Pictorial View of Combustion Unit	9
2. Pilot Plant Flow Diagram	10
3. Thermocouple Location and Temperature Profiles	12
4. Effect of Excess Air On Residence Time	13
5. SO_2 Sample Train	15
6. Particulate Collector and Gas Sample Switchbox	17
7. Wet Train SO_2 Analysis	18
8. Crushing, Sizing and Injection System	24
9. Effect of Additive Feed Rate	28
10. Effect of Injection Air Velocity	33
11. Effect of Temperature and Particle Size on Calcination	37
TABLES	
I. Typical Flue Gas Analysis	8
II. Anclysis of Injection Material As Received	21
III. Coal-Limestone Mixture	32
IV. Comparison of Reacted Material Sulfur Analyses	35

TABLE OF CONTENTS CONT'D

		PAGE NO.
V.	Red Mud Injection Test Data	41
VI.	Red Mud Chemical Analysis	42

SUMMARY

This report covers work completed under National Air Pollution Control Administration Contract PH-22-68-68 during the period from June 26, 1968 to June 1, 1969. Tests were made to evaluate the effectiveness of six selected solid sorbent materials in removing sulfur dioxide (SO_2) from coal combustion gases in a chain grate-fired furnace. Effects of additive feed rate, particle size, and injection temperature were studied. Calcination* and calcium oxide utilization** were determined.

The combustion unit is a chain grate stoker 3 feel wide and 17 feet long with an effective grate area of 45 square feet that accommodate coal-firing rates up to 450 pounds per hour. Western Kentucky seam Number 11 coal containing 3.14 per cent sulfure was burned during the majority of the tests.

The sorbents used in this investigation were an aragonite, a calcite, two types of dolomite, and a chalk. "Red mud," the dried tailings from the manufacture of alumina from bauxite, was also tested.

Sulfur dioxide removal ranged from 6 to 65 per cent depending upon operating conditions. Sorbents compared on a per-unit-weight-of-raw-stone basis show that the calcites and aragonite removed greater amounts of SO_2 than the dolomites. Sorbent 1683, an aragonite, was the most effective of all materials tested when injected into the gas stream. However, it was relatively ineffective when mixed with the coal prior to combustion. It was found that SO_2 removal increases with increasing sorbent feed rates.

*Heating to a temperature where carbon dioxide is expelled.

**The weight of calcium oxide as calcium sulfate in the reacted additive with respect to the weight of calcium oxide injected.

The particle size study was not as definitive as desired due to overlapping particle sizes between injected screen cuts. A step-wise regression analysis of 59 runs with samples 1337 and 1684 (dolomite), 1683 (aragonite), and 1359 (calcite) combined, indicates that reducing the sorbent particle size can be expected to lead to higher SO_2 removal rates.

Each of the sorbents, except red mud, was injected at temperatures from 1800°F to 2450°F. Computer results on all test data combined did not indicate a significant correlation between SO_2 removal and injection temperature. However, graphical analysis did indicate that temperature was a significant parameter for some of the individual samples.

The degree of sorbent calcination varied directly with temperature and ranged from 50 to 60 per cent at 1800°F to greater than 90 per cent at 2450°F. Above 2000°F particle size did not appear to significantly affect the degree of calcination.

Calcium oxide utilization varied from 6.30 per cent for particle sizes greater than 100 mesh to 59.50 per cent for -200 mesh sizes. Sample 1683, the aragonite, and sample 1684, a dolomite, demonstrated the greatest utilization.

Red mud, when injected into the gas stream at 1200°F to 1300°F and 2000°F was relatively ineffective in removing SO_2.

CONCLUSIONS

The following conclusions are based on data accumulated from tests made in a pilot chain grate furnace. The data may have possible limitations, however, every effort has been made to interpret the results as they may apply to full scale field injection tests.

1. Maximum sorption was reached within 0.5 to 0.75 seconds at an injection temperature range of 2000°F to 2450°F.
2. Sulfur dioxide removal varies directly with additive feed rate and injection velocity.
3. Optimum additive particle size determinations could not be ascertained from the tests. However, it is concluded that particle size reduction will increase SO_2 removal.
4. Characterization of injection materials is required to achieve maximum SO_2 removal.
5. Calcination varies directly with injection temperature. Sorbent particle size does not significantly affect calcination at temperatures above 2000°F. Greater than 90 per cent calcination was attained at an injection temperature range of 2400°F to 2450° F.
6. The rate of formation of calcium oxide within the temperature ranges tested is not a limiting factor in sulfur dioxide removal.
7. Calcium oxide utilization ranged from 6.3 per cent for particle sizes greater than 100 mesh to 59.5 per cent for -200 mesh sizes.
8. Generally, -200 mesh injected material gave the best sulfur balances as a result of the particulate sampler design. Flyash contamination in the reacted samples presented a problem in making sulfur balances.

9. Sorbent mixed with the coal prior to combustion was not as effective for SO_2 removal as injecting sorbent into the gas stream.

10. Red mud was not effective in reducing SO_2 when injected into the gas stream.

11. The sulfate form of the sulfur was the only significant form present in the reacted material.

12. At injection temperatures above 2000°F, sample 1683 was most effective by removing 30 to 60 per cent of the SO_2; followed by sample 1684 (20 to 60 per cent); sample 1337 (20 to 45 per cent); sample 1359 (20 to 45 per cent); and sample 2077 (20 to 40 per cent).

13. Sorbents compared on a per-unit-weight-of-raw-stone basis indicate that the calcites and aragonite remove more SO_2 than the dolomites.

RECOMMENDATIONS

The following recommendations are made:

1. Further characterization of each sorbent is needed to optimize injection temperature, particle size, and injection rate. After a screening criteria is established, conduct studies with a larger number of materials.
2. Study a wide range of injection velocities and dispersion patterns for effects upon SO_2 removal.
3. Investigate the tendency of limestones to disintegrate under the severe temperature shock conditions normally found in boiler injection processes.
4. If possible, future investigations should employ trend data analysis. In this manner it becomes possible to follow the trends of a sorbent and more completely and economically analyze the characteristics of the material.
5. Design experiments to specifically study combination effects such as residence time - temperature, particle size - temperature, etc.
6. Crushing characteristics of sorbents should be studied more closely to obtain data for economic studies.
7. Full scale tests should be made by injecting sorbents into the furnace at 2200°F to 2400°F in amounts from 1 to 2 times stoichiometric. Injection velocities should be great enough to obtain maximum dispersion and furnace gas penetration.

ACKNOWLEDGEMENT

The authors wish to thank all who contributed to this project within the National Air Pollution Control Administration, Tennessee Valley Authority, Bituminous Coal Research, Inc., and Commercial Testing and Engineering Company. A special acknowledgement is given to Peabody technicians James Smith and Jerry Corbin.

INTRODUCTION

Many efforts[1] from bench-scale to large commercial-scale investigations are being made to combat air pollution that is attributed to large coal-burning utilities. This project is intended to contribute to the various investigations as an intermediate scale study and to explore the applicability of dry additives to smaller than utility size industrial boiler installations.

Six selected additives were reacted in a chain grate-fired pilot plant. The combustion unit was selected because of the relatively small amount of flyash found in the flue gases, the relatively isothermal conditions with no steam production, and the residence time comparable to some commercial installations. The additives were selected in order to compare differences between calcites and dolomites.[2] The materials consisted of an aragonite, two calcites, and two dolomites. Red mud, the dried tailings from the manufacture of alumina from bauxite, was also studied. A chalk was included as one of the calcites because of its ease of grinding and high reactivity with sulfur dioxide. All additives were selected on the basis of work previously completed by the National Air Pollution Control Administration.[3]

The effects of additive feed rate, particle size, and injection temperatures were studied. The rate of calcination[2] and calcium oxide utilization were determined.

PILOT PLANT APPARATUS

The combustion unit used in these studies was a pilot moving-grate coke furnace, shown in Figure 1. The flow diagram is shown in Figure 2. The unit consists of a chain grate 3 feet by 17 feet with an effective grate area of 45 square feet. Combustion gases pass from the furnace through a rectangular refractory duct 1.25 by 3 feet, to a cylindrical 14-inch diameter duct. The gases are quenched with water at a point about 44 feet

from the grate and routed through a baghouse or by-passed to the atmosphere. The large bag filter was not used because of the unknown effects of the quench water sprays on the reacted additives.

Gas sample points are located at various levels in the cylindrical duct in front of the spray cooling section in order to monitor the flue gas and study the reaction rate between the injected material and the SO_2 in the gases. A particulate sample system was installed at a point in the reactor 38 linear feet from the grate level.

The combustion unit can accommodate coal-firing rates up to 450 pounds per hour. Gas flows in the system reached 1300 SCFM (wet). A typical analysis of the gas at 80 per cent excess air is shown in Table I.

TABLE I

TYPICAL FLUE GAS ANALYSIS

Mole %	Wet	Dry
CO_2	9.50	9.96
H_2O	4.59	----
SO_2	.16	.17
N_2	76.88	80.58
O_2	8.80	9.22
CO	.07	.07
	100.00	100.00
Mol. Wt.	29.47	30.01

Coal was supplied to the unit from a coal storage bin located directly above the furnace. The coal was sampled by traversing the discharge chute at the end of the belt conveyor supplying the storage bin. The feed rate of the coal was regulated by means of a movable gate that controlled the depth of the coal on the moving grate. Primary combustion air was supplied through the moving grate, and secondary air was added directly to the flame area above the fire bed.

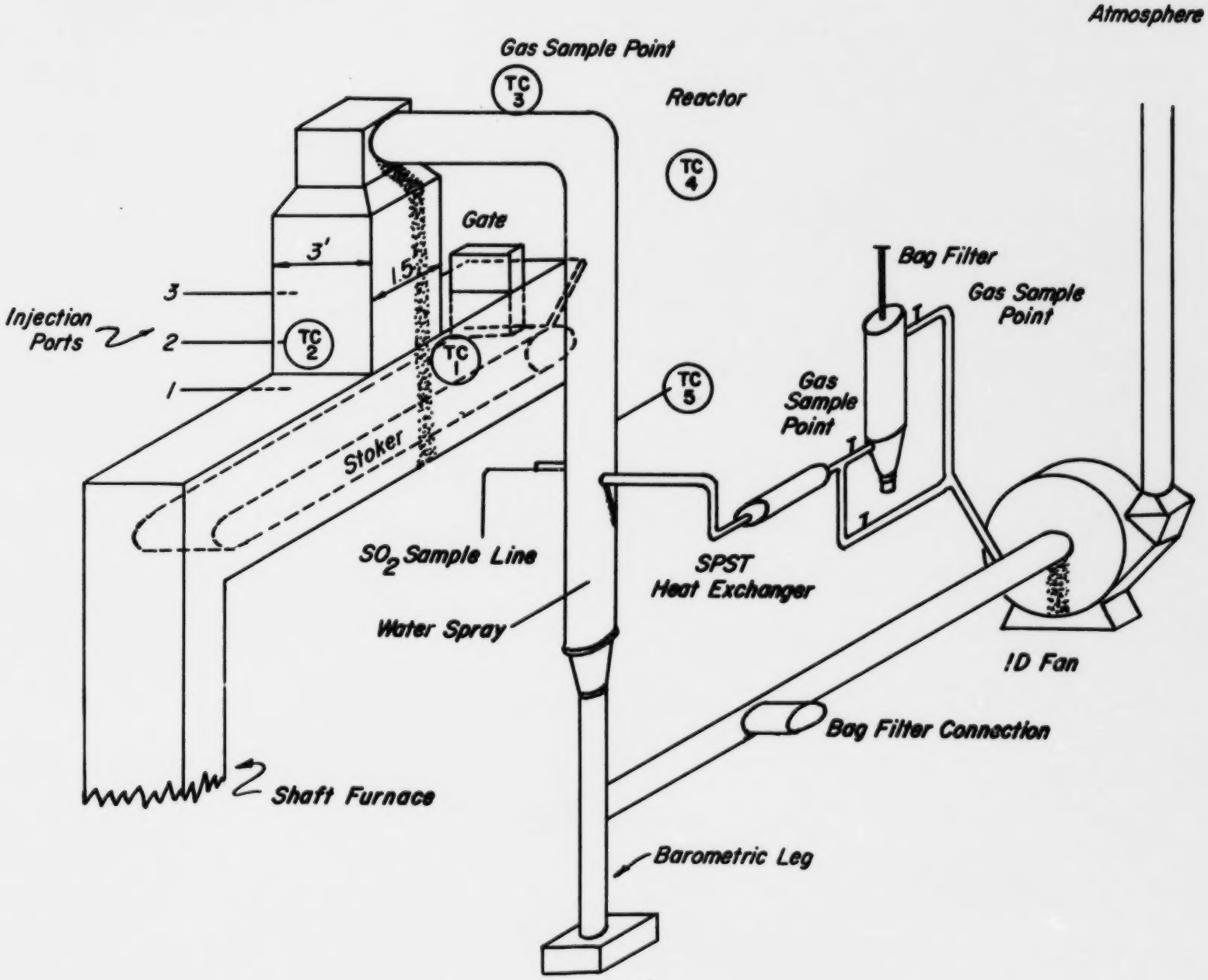
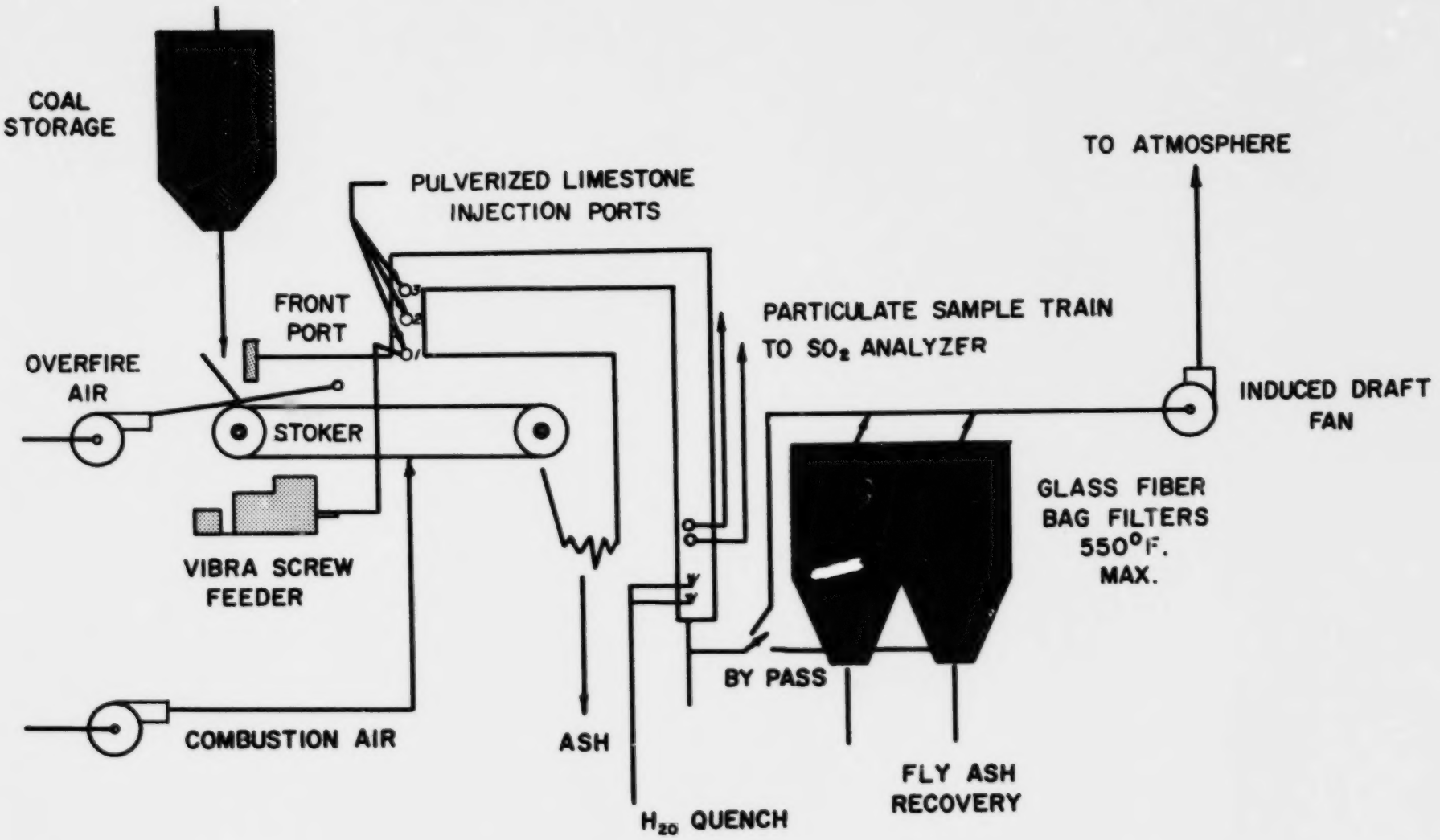


Fig. 1 Pictorial View of Combustion Unit



FLOW DIAGRAM
OF
INJECTION STUDIES
Figure 2

Temperature was monitored by thermocouples located throughout the unit. The temperature profiles at various coal feed rates are shown in Figure 3.

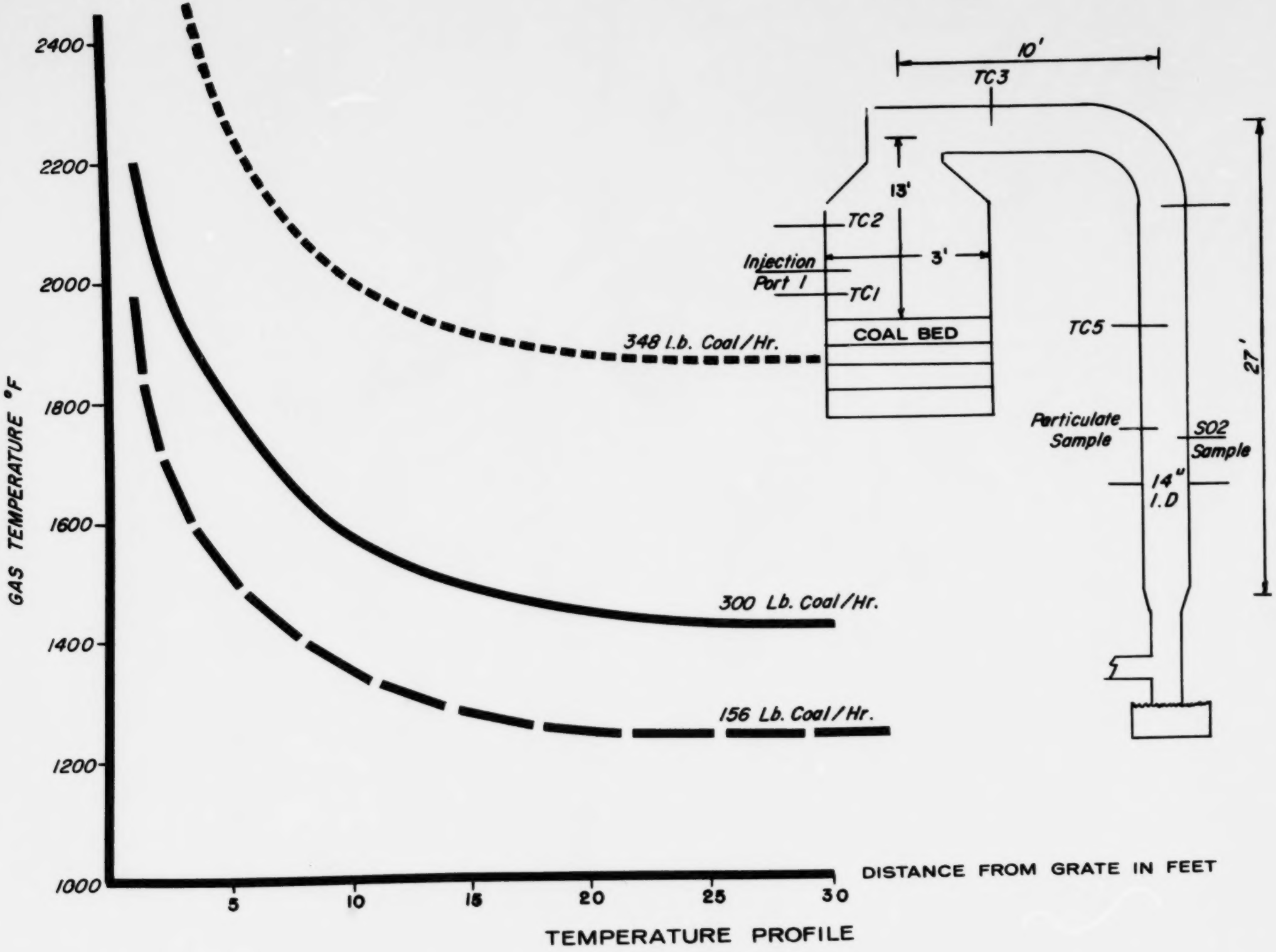
Injection ports were located vertically in the rectangular section leading to the cylindrical duct. An additional port was located toward the front of the furnace where the 2400°F to 2500°F injections were made.

The furnace was not equipped with a standard ash discharge, but did have a shaft furnace that was used in coke production. This prohibited the sampling of the total ash from each run; however, by sampling the grate before it dumped into the shaft furnace, it was possible to get ash samples.

System Velocities and Residence Time

Because of existing system design and temperature, actual measurement of system velocities was impractical. Therefore, values were calculated. The calculated velocities are accurate because system dimensions, flow rates, and input and output materials are known.

At a given coal feed rate, temperature and residence time in the furnace are a function of per cent excess air (see Figure 4). Furnace residence time is defined as the time required for the additive particles to travel from the injection point to the water quench point assuming the particles travel at the velocity of the combustion gases. Total residence time at a maximum coal feed rate of 348 pounds per hour ranged from 0.3 seconds to 0.6 seconds depending upon per cent excess air. At a coal feed rate of 185 pounds per hour, total residence time ranged from 1.08 seconds to 1.35 seconds (see Figure 4). Velocities in the rectangular combustion chamber where the injections were made ranged from 9.9 feet per second at the lowest coal feed rate to 25 feet per second at the highest coal feed rate. Residence times presented



TEMPERATURE PROFILE

FIG. 3

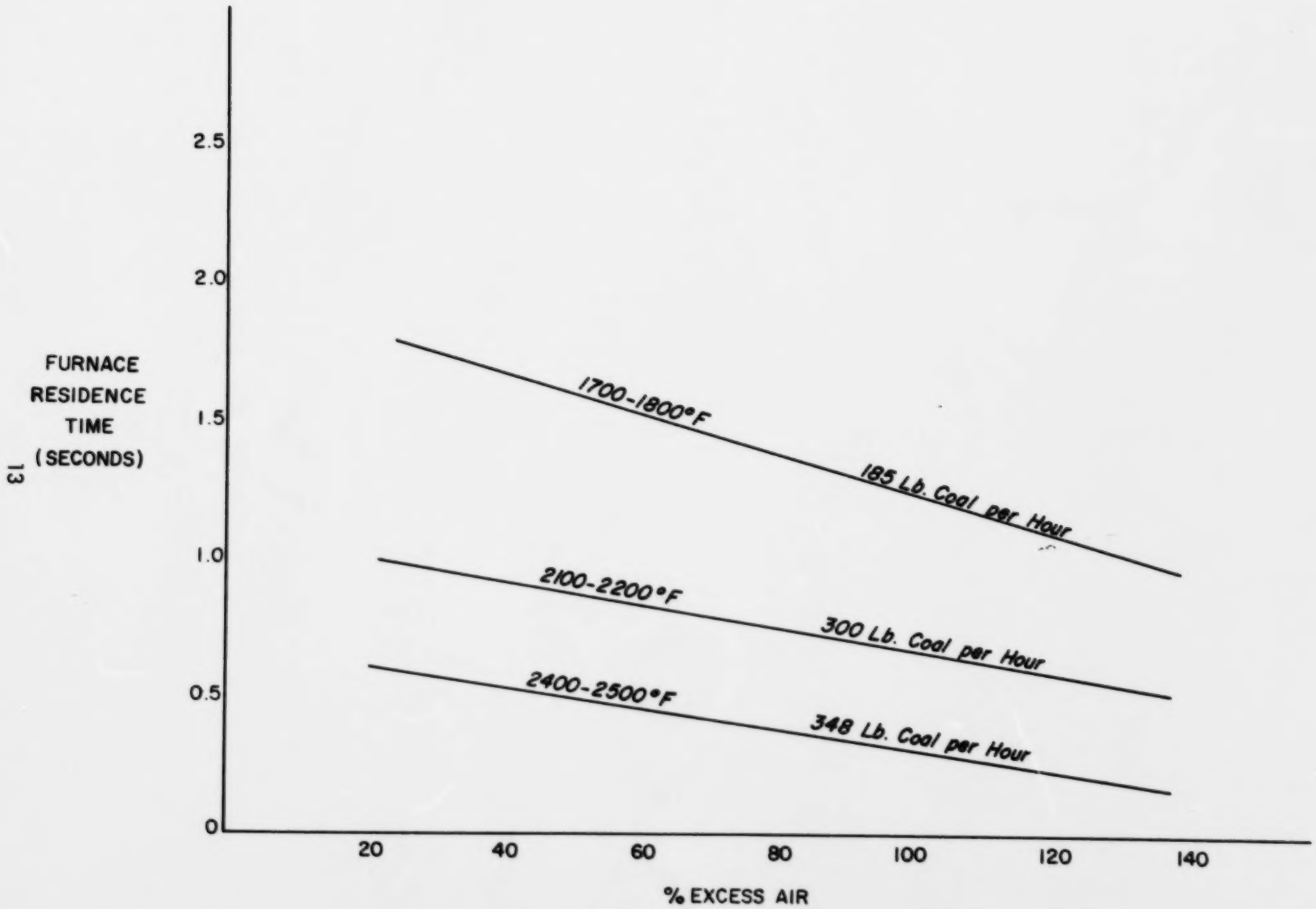


Fig. 4

Effect of Excess Air Based on Calculated Residence Time

are minimum and do not allow for any increase due to mixing turbulence, etc.

Combustion calculations were standard and were made according to Lewis, Radash, and Lewis;[4] Potter;[5] and Hougen, Watson, and Ragatz.[6]

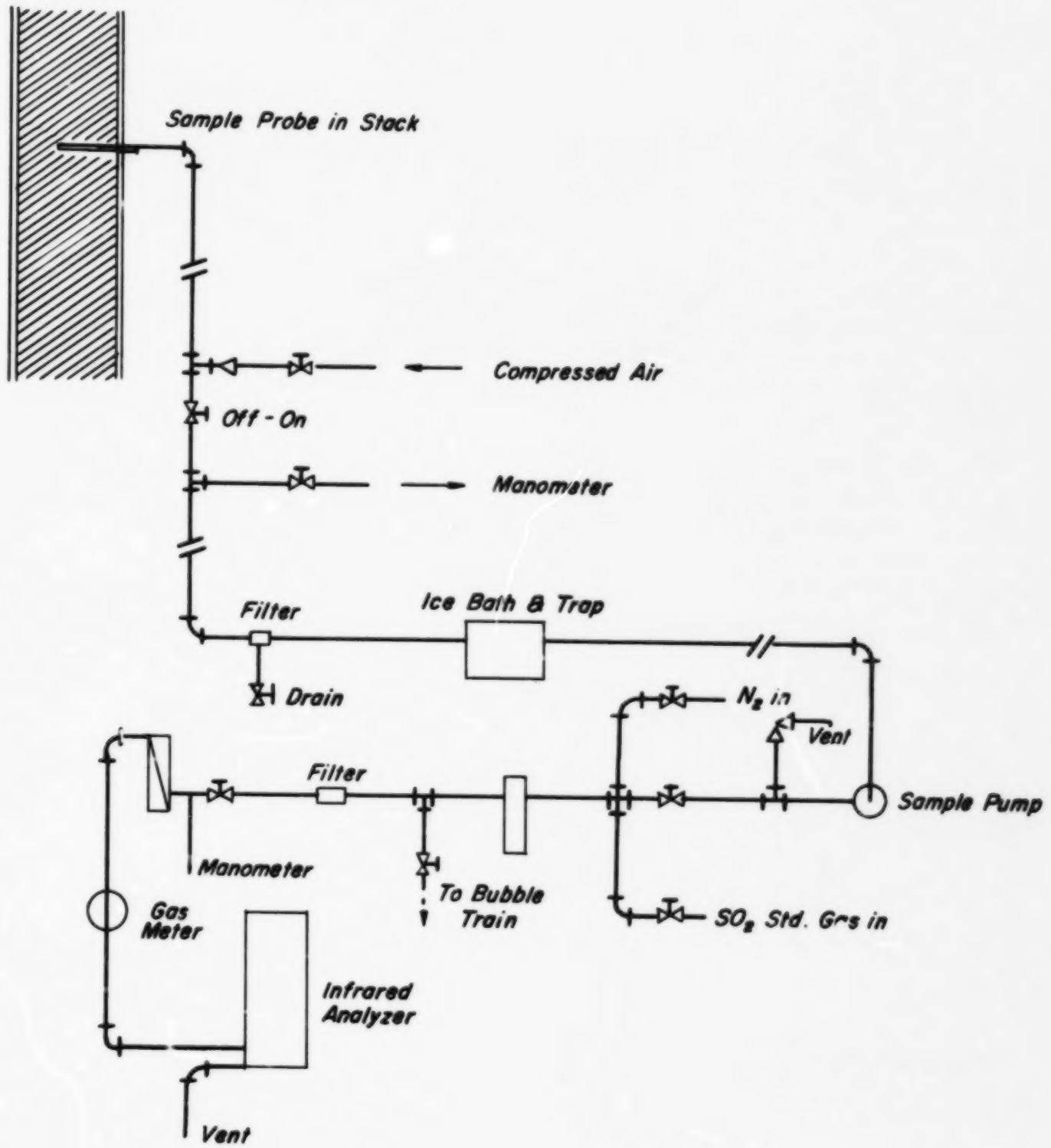
Injector Design

The injection apparatus consisted of a modified sandblasting gun that was attached to the furnace injection ports by means of a pipe union. It was operated with 250°F compressed air. The sandblaster was modified by attaching a section of schedule 40, 1/4-inch pipe long enough to extend through the furnace wall four to six inches.

The injection air volumes were controlled at a constant 640 SCFH. The air rate was established by injecting the various sizes of material at the maximum estimated input. The 640 SCFH is about one per cent of the total combustion air required and does not take into account the small amount of conveying air that is induced to convey the stone from the feeder to the injector nozzle. This relatively small amount of air was advantageous because the temperature of the furnace gases was not significantly lowered at the point of injection, and minimum residence time was required for additive and air heat-up. Air-to-limestone ratios ranged from 7:1 to 1:1.7. The injections were made into a rectangular duct with a cross-sectional area of 3.75 square feet and were directed across the 3-foot dimension of the duct at right angles to the flow of the combustion gases (see Figures 1 and 3).

Gas Sampling System

A schematic of the gas sampling train is shown in Figure 5. The sample probe was a 1/2-inch, stainless steel, open-end pipe inserted to the center of the 14-inch diameter reactor. A six-foot length of 1/4-inch stainless tube was connected to the



Sulfur Dioxide
Sample Train
Figure 5

probe in order to cool the gases before they entered a 3/8-inch polypropylene tube 20 feet long. The gas passed through the tube to a panel board located in front of the pump. The panel board contained a manometer to check line plugging, a glass wound micro filter to remove entrained moisture and particles, and a compressed air valve to clear the line connecting to the sample probe.

The clean gas then entered three Erlenmeyer flasks connected in series that were packed in ice. At this point almost all of the moisture was removed from the gas. The gas was then pumped another 46 feet to the panel board in the laboratory. This panel board measured gas volume and pressure, permitted the standard and zero gas to be connected to the system, allowed the connecting of supplementary wet test equipment as well as the Model 315-A Beckman Infrared Analyzer. Calculated response time was 46 seconds from sample point to the analyzer.

The system also contained a switch box arrangement shown in Figure 6. This innovation provided a quick method of changing sample points in the reaction system as well as a method for determining any losses in the particulate sample collecting arrangement.

Wet Test Gas Analysis

A back-up apparatus for gas analysis was used as a check against the infrared instrument. Cooled stack gases were passed through a 3 per cent solution of hydrogen peroxide. The sulfur dioxide reacted with the peroxide to form a dilute solution of sulfuric acid which was then titrated with a dilute standard solution of sodium hydroxide. The equipment layout is shown in Figure 7.

Particulate Sample System

Initially, the plan was to sample the entire gas system for particulates.

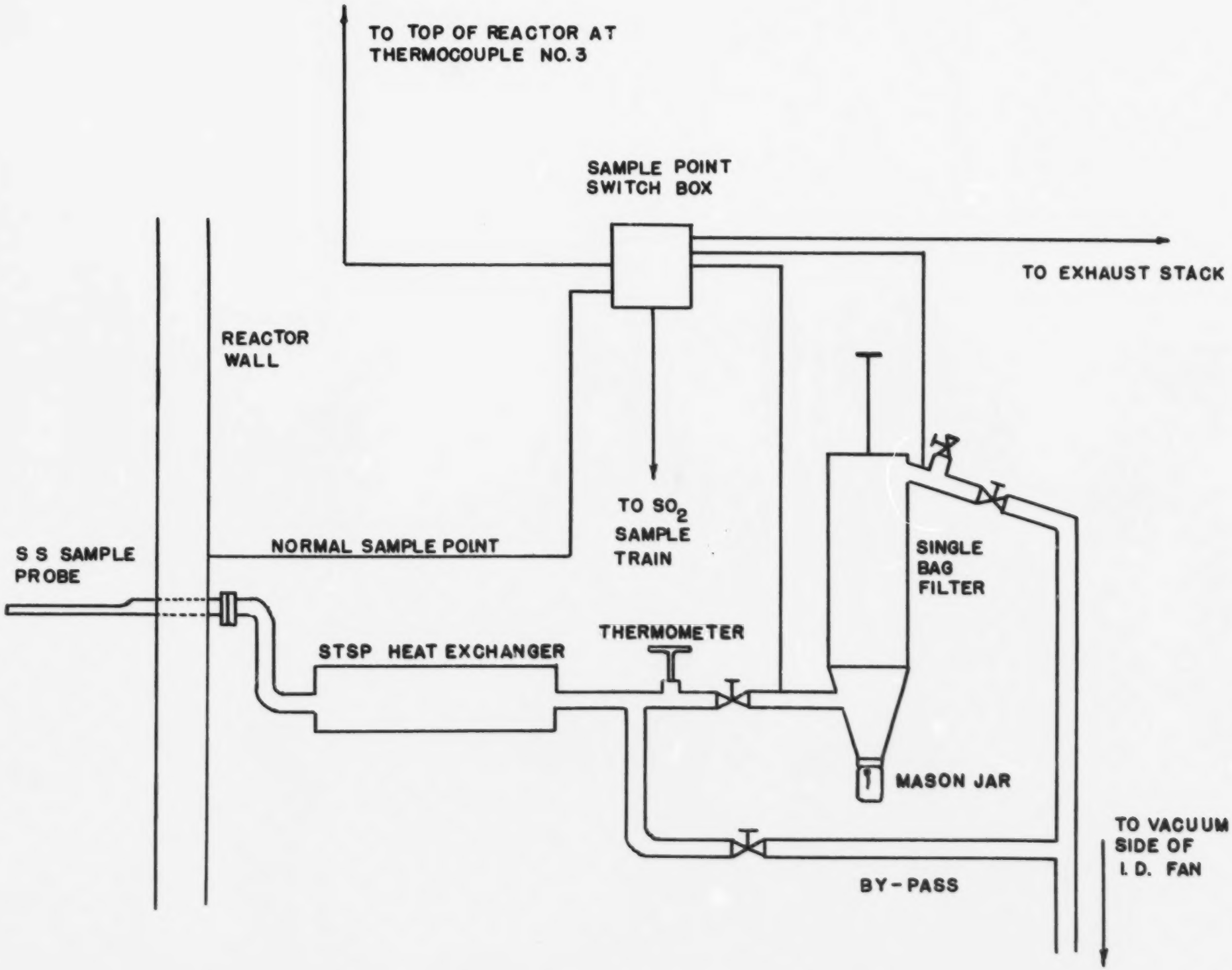
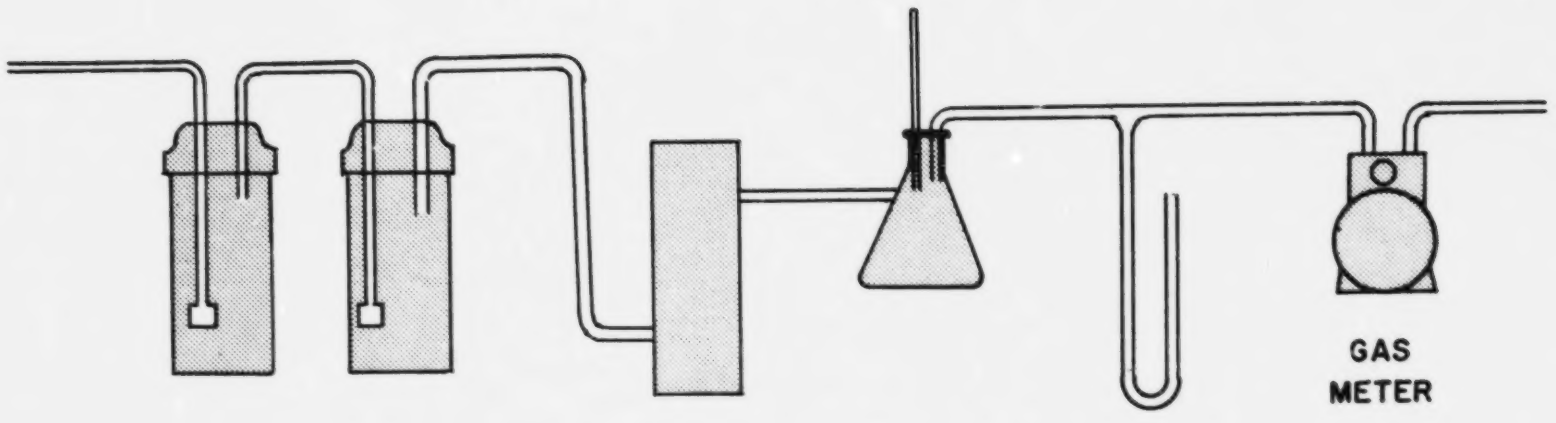


FIGURE 6 PARTICULATE COLLECTOR AND GAS SAMPLE SWITCHBOX



WET TRAIN SO_2 ANALYSIS

Figure 7

However, this was not feasible because cooling water sprays were located in the reactor in order to cool the flue gases to 500°F. The water quench caused the injected sorbent to either wash into the drip leg or to agglomerate in the ducts leading from the reactor drip leg to the exhaust fan.

Since it was not possible to obtain total sampling, it was decided to partially sample the gas stream before it reached the cooling section. This procedure was only moderately successful. A decision was made to design the largest probe with the greatest exposed collecting area that the side entrance to the reactor could accommodate. The opening was a pipe flange 2-1/4 inches in diameter. The flange permitted a 2-inch pipe to slide in the reactor and a 2-1/4 inch sleeve suported the probe as well as sealed the joint from outside air. The probe was fabricated by taking a 2-inch stainless schedule 40 pipe and fashioning a shovel face. The face was shaped by splitting the pipe vertically and exposing the greatest width or cross-sectional diameter to the downward flow of the flue gases in the reactor.

With the shovel face inserted to a depth of 12 inches across the reactor, it was possible to sample approximately 16 per cent of the total reactor cross-sectional area. The gases then passed through a single tube-single pass heat exchanger for cooling to below 500°F. Flow of gases was provided by a vacuum produced when the by-pass arrangement was connected to the input side of the induced draft fan. The collector was a single fiber glass bag filter housed in a 10-inch pipe. The base of the pipe is fitted to a funnel which was attached to a screw top glass jar used as a receiver for the material collected in the bag (see Figure 6).

The by-pass piping was arranged to permit the bag filter to be taken out of the sample circuit and emptied by both mechanical shaking and back flow of air at the

top of the bag. A thermometer located in the pipe in front of the bag filter was used to monitor temperatures and to prevent high temperature gases from destroying the bag filter.

TEST MATERIALS AND PREPARATION

Injection Materials

Six injection materials were selected for this study as a result of the fixed-bed capacity studies[3] completed by the National Air Pollution Control Administration in Cincinnati, Ohio. The materials, as defined by Boynton,[2] included one calcite, sample 1359; one aragonite, sample 1683; two dolomites, samples 1337 and 1684; one chalk, sample 2077; and red mud.

All the materials except red mud had high capacity for SO_2 in the fixed-bed sorption tests. The calcites and dolomites were selected to determine if differences between the two types of materials existed. The samples represented materials found in Ohio, Virginia, Pennsylvania, Texas, and the Bahama Islands (see Appendix B, page B-4). The chalk was selected for comparison because of its high capacity for SO_2 in the fixed-bed tests and its ease of grinding. The chalk sample used in these tests came from Texas. Red mud was selected for testing because of reports of relatively high SO_2 removal rates at temperatures less than 1200°F.[7]

The materials were ordered from commercial suppliers and were not a part of the reserve samples that were tested in NAPCA fixed-bed sorption tests. A comparison of the chemical analyses of materials used in tests reported herein and the materials used in the fixed-bed sorption tests is shown in Table II.

It was not within the scope of this contract to make an investigation of physical characteristics of the samples; however, each material was found to have some physical

TABLE II

ANALYSIS OF INJECTION MATERIAL AS RECEIVED

PER CENT BY WEIGHT OF IGNITED SAMPLE 900°C

Sorbent Number Source of Analysis	1359 CT&E*	1359 BCR**	1684 CT&E	1684 BCR	1337 CT&E	1337 BCR	1683 CT&E	1683 BCR	2077 CT&E	2077 BCR
Loss on Ignition	43.37	43.60	46.91	46.30	46.60	47.50	44.47	44.20	44.67	39.80
Silica, SiO_2	2.44	1.07	2.61	2.25	0.92	0.77	0.56	1.10	10.14	9.60
Ferric Oxide, Fe_2O_3	0.28	0.22	0.64	0.72	0.00	0.24	0.14	0.10	1.63	1.74
Lime, CaO	93.93	97.00	56.03	58.00	55.80	54.00	96.54	96.20	81.46	83.00
Magnesia, MgO	1.54	1.16	39.17	37.50	41.55	43.50	0.72	0.80	0.99	0.64
Sulfur Trioxide, SO_3	0.37	---	0.39	---	1.08	---	0.85	---	0.09	---
Undetermined	1.44		1.16		0.65		1.19		5.69	3.46

* CT&E - Commercial Testing and Engineering, Inc., Birmingham, Alabama

** BCR - Bituminous Coal Research, Inc., Monroeville, Pennsylvania

characteristic that affected its ease of utilization in some portion of the evaluation.

Sample 1359, a calcite, was received in paper bags. Ninety per cent of the material as received was less than 100 mesh size and tended to compact easily. A high surface attraction was apparent. The material was very difficult to screen and tended to plug the fine screens. The fine -200 mesh material was almost impossible to inject in amounts greater than 100 per cent of stoichiometric with the existing injector design.

Sample 1337, a dolomite, was received in paper bags and identified as an agricultural grade material. The material as received contained 80 per cent -100 mesh size and was very easily screened. Injection of the material was accomplished without difficulty as a result of little surface attraction between the particles.

Sample 1684, a dolomite, was received in paper bags. It was identified as an agricultural grade and contained about 70 per cent -100 mesh as received. The material tended to pack and was difficult to screen and inject at rates greater than stoichiometric with the existing injector design. The handling characteristics resembled those experienced with sample 1359.

Sample 1683, an aragonite, was received in drums and contained only about 20 per cent -100 mesh material. Pulverizer throughput was reduced to 25 per cent of capacity when compared to throughput of the other sorbents. Once pulverized, the material separated well and was easy to handle.

Sample 2077, a chalk, was received in paper bags that were packed in burlap bags. The material was wet enough to cause the paper bags to tear easily, and drying was required prior to crushing. Greater than 92 per cent of the chalk as received was +100 mesh size. After drying, the material was easily pulverized but tended to pack.

Handling characteristics were comparable to sorbents 1359 and 1684.

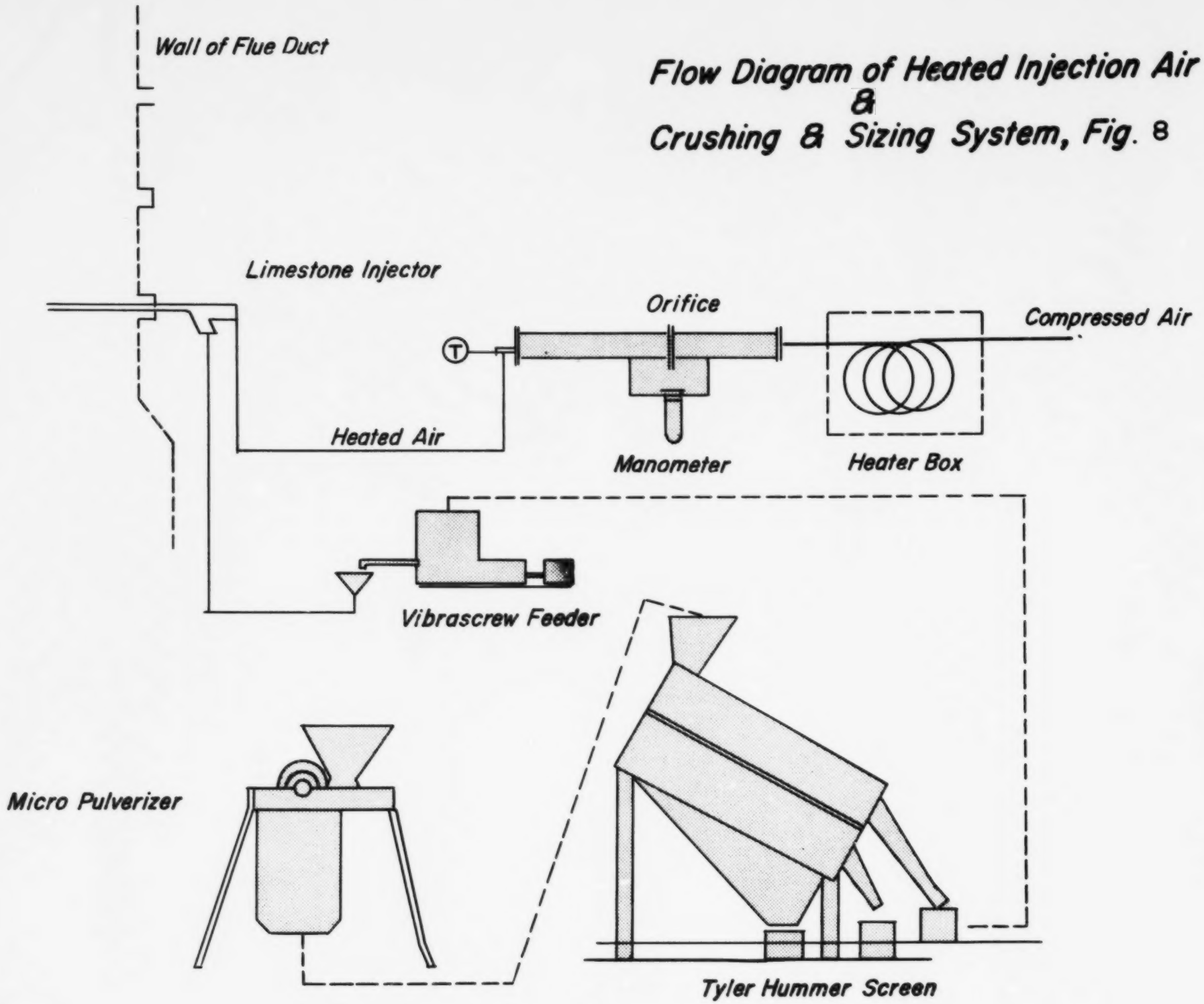
Red mud was received in hardboard barrels and contained about 75 per cent -50 mesh material. Screening could not be accomplished because of screen plugging. The material was difficult to feed to the injector because of a tendency to pack.

All screening was done on a Tyler-Hummer vibrating screen. This is a two-screen small industrial unit which provides three cuts of screened sorbent: oversize, middle cut of -140 +200 mesh size, and the bottom cut of -200 mesh as mentioned previously.

The original objective of the program was to inject three distinct particle sizes, -50 +100 mesh, -150 +200 mesh, and -325 mesh, with 70 per cent of the total injection material in the defined size range. Because of the quantity of limestone required and lack of screen efficiency, the original size plan was not accomplished. Other screens for the Tyler-Hummer unit were purchased but did not improve efficiency to the point desired. It was then decided to inject "as received" material, -140 +200 mesh cut and -200 mesh cut as screened on the Tyler unit. Figure 8 depicts the flow of material through each stage of preparation and separation.

Samples 1359, 1337, and 1684 as received were screened prior to pulverizing in order to separate the sizes less than 140 mesh into -140 +200 mesh and -200 mesh cuts. The +140 mesh was then pulverized with a micro pulverizer and screened into the -140 +200 and -200 mesh cuts and blended with the first separation material. Samples 1683 and 2077 and the red mud had to be pulverized before screening. However, the red mud did not lend itself to screening, and it was injected into the furnace as received. Sample 2077 was so soft that it was reduced to greater than 70 per cent passing through a 200-mesh screen with only a small amount of -100 +200 mesh material.

Flow Diagram of Heated Injection Air & Crushing & Sizing System, Fig. 8



Test Coals

Two coals were selected for the tests. Western Kentucky coal, Number 11 seam, washed and sized to 1-1/2 inch by 28 mesh, was used for most of the tests. Sulfur content was in excess of 3 per cent. An average analysis is presented in Appendix B, Table B-1.

Four tests were made with southern Illinois Stonefort coal containing 4.47 per cent sulfur as received to study the effects of SO_2 concentration in the flue gas on SO_2 removal. An average analysis is presented in Appendix B, Table B-2. The coal had greater than 20 per cent ash and was of such a size (1-1/2 inch top size by 0 bottom size) that burning to completion on the moving grate required greater amounts of combustion air than the Number 11 Western Kentucky coal normally required. The SO_2 concentration was therefore diluted to about the same level as the flue gas from the burning of the Western Kentucky coal, thereby making the tests unsuccessful in determining SO_2 concentration effects.

EXPERIMENTAL RESULTS AND DISCUSSION

Data obtained from the experimental tests are presented in Appendix A. The results of the tests were carefully studied by graphical analysis. In addition, several cases were studied by computer using step-wise regression analysis. In interpreting the results of the computer studies, a 95 per cent confidence level was arbitrarily selected to determine if a particular relationship was significant.

A listing of simplified definitions of the most important terms used throughout this section in discussing the computer results is presented in Appendix C, page C-2.

SO_2 Sampling Points

It was necessary to check SO_2 levels at several points in the exhaust system to

determine if any SO_2 was being removed in the bag filter and other points. This was accomplished by constructing a switchboard consisting of sample tubes connected with female quick dis-connect units and one male unit that could be plugged into the desired sample line and could also be connected to the sample line leading to the analyzer train (see Figures 3 and 6).

The sample gas lines were connected as follows:

1. To a point where the reactor connects to the rectangular duct from the furnace at thermocouple number 3.
2. To a normal sample point on the reactor adjacent to thermocouple number 5.
3. To a point on the gas-particulate pipe prior to the bag filter.
4. To a point on the gas vacuum line just after the bag filter.
5. To the exhaust stack on the output side of the induced draft fan.

Little reaction occurred between the point where the reactor connects the rectangular duct and the normal sample point (i.e., thermocouple number three and thermocouple number five), indicating that most kinetic reactions are completed between the point of injection and a point within the furnace in a time of one second or less. This may be due to the initial physical-chemical reaction taking place at the point of calcination and has been reported previously by Kruel and Juntgen.[8]

During operation of the furnace, the infrared recorder measured a response to the sorbent within one minute after beginning the injection into the gas stream. After stopping the injection, a response was recorded within one minute. Also, the recorder returned to the original base line before injection within three to four minutes. This observation, along with the fact that inspections of the furnace walls revealed

negligible deposits, suggests that most of the measured SO_2 removal was due to gas phase reaction. Substantial wall effects have been reported by Ishihara.[9]

To check for any removal in the bag filter, a series of checks were made starting with blank runs at the set temperature. Sampling the gases entering and leaving the bag filter produced data that indicated dilution of the gas from an opening used for the shaking apparatus in the particulate sample collector. There was no difference in the SO_2 reading between the normal sample point and the point on the sample line leading to the bag filter, but a slight SO_2 decrease was experienced at the point after the bag filter.

The above experiment was repeated while injecting sample 1337 as received. The SO_2 concentration at the normal sample point was the same as at the point just prior to the filter. When the dilution factor from the blank run was applied to the data taken at the point after the bag filter, no further SO_2 removal was indicated.

A further check was made at a point on the exhaust side of the induced draft fan about 30 feet up the stack from the fan. At this point all gases and particulate were cooled to below 500°F by water sprays located in the reactor or cylindrical duct about 10 feet below the normal sample point. Again, no further SO_2 removal occurred.

Effect of Additive Feed Rate

The literature [1, 8, 9] indicates that SO_2 removal is increased as additive feed rate is increased at a given temperature and particle size. Tests were made while varying the additive feed rate of sample 1683. Results are shown in Figure 9. It was assumed that additive samples 1359, 1337, 1684 and 2077 would produce the same general effects and the decision was made to maintain most tests at near

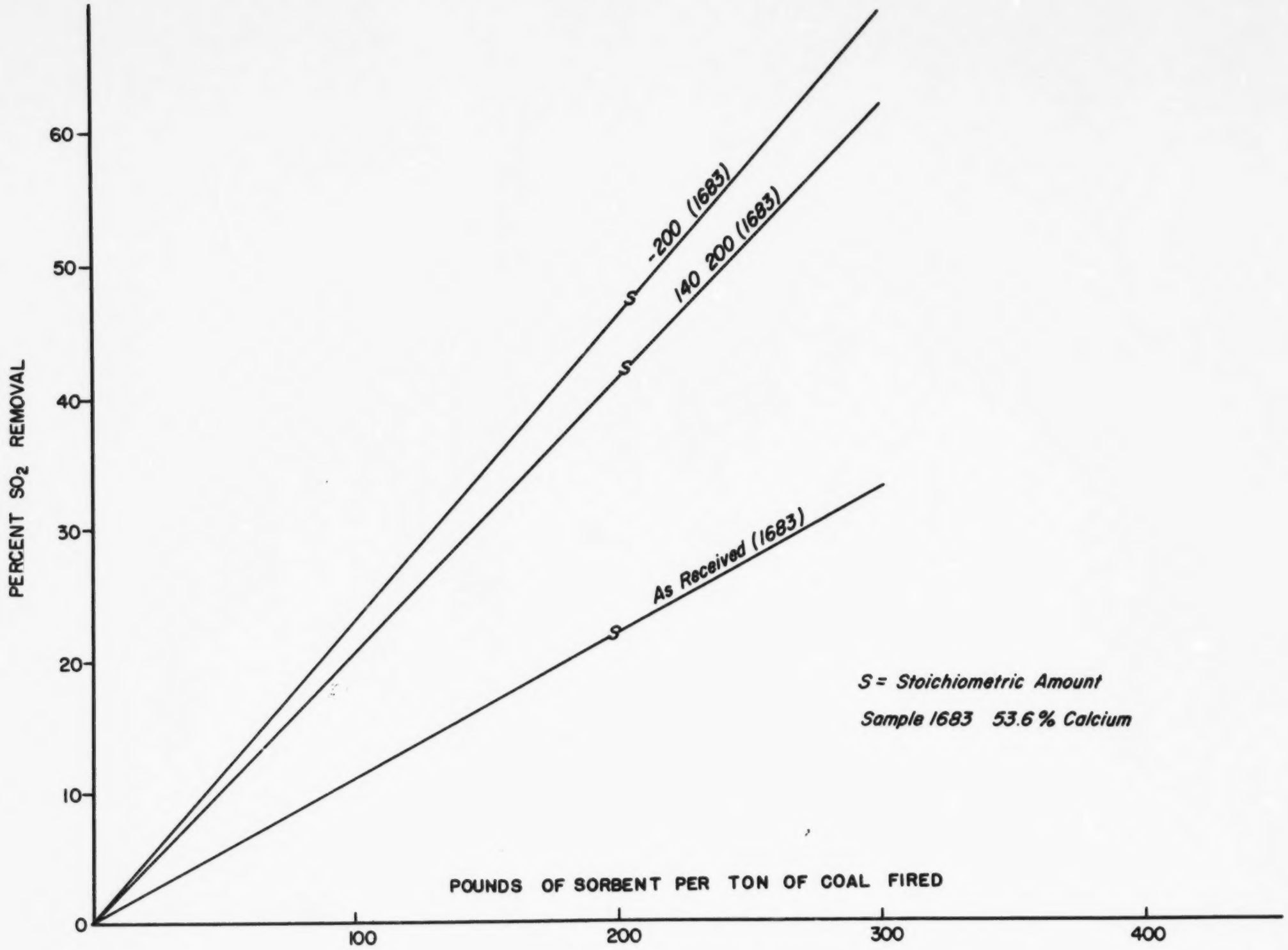


FIGURE 9 EFFECT OF ADDITIVE FEED RATE

stoichiometric amounts.

A step-wise regression analysis of the results from 59 runs with samples 1337, 1359, 1683 and 1684 combined, confirmed that the increased additive feed rate or stoichiometry leads to increased SO_2 removal.

Effect of Particle Size

As previously discussed, the original test plan specified three particle size ranges of each sorbent, except red mud, to be injected into the flue gas to determine the effects of varying the particle size. A minimum of 70 per cent of the material was desired in the ranges of -50 +100 mesh, -150 +200 mesh and -325 mesh. This plan was not accomplished due to quantity of limestone required and lack of screen efficiency. As received material, -140 +200 mesh and -200 mesh cuts as taken from the Tyler-Hummer screen were decided to be the sizes for injection. However, this proved not to be as definitive as hoped for because many of the cuts with some of the materials were too near the same size. This prevented direct comparisons of materials for effect of particle size and did not produce data that would conclusively indicate optimum sizes. The tabulated screen size data is presented in the Appendix A, page A-4.

If the log mean of the mesh openings of screen sizes are plotted against weight per cent of material passing indicated sizes, on probability graphs, the variation of sizes may be seen as shown in Appendix A, Figures A-1 through A-5.

An examination of plots of per cent SO_2 removal at stoichiometric feed rates versus screen openings through which 50 per cent of the material passed (a sample figure is shown in Appendix A, Figure A-6) indicate that no general trends are demonstrated that can be correlated to particle size except in the case of sample 1683.

However, plots of per cent SO_2 removal versus weight per cent of material retained on a given mesh size indicate in some cases that removal rates may be correlated to particle size. (A sample figure is shown in Appendix A, Figure A-7.) Graphical analysis of samples 1683, 1684, and 2077 data indicates that SO_2 removal was increased as particle size was decreased (See Appendix A, Figures A-7, A-8, and A-9). Samples 1359 and 1337 SO_2 removal data could not be correlated to particle size (See Appendix A, Figures A-10 and A-11).

A step-wise regression analysis of 59 runs with samples 1337, 1359, 1683 and 1684 combined, resulted in a negative correlation coefficient value for particle size. This suggests that grinding the sorbents can be expected in general to lead to higher SO_2 removal rates. It was found that the correlation coefficient was about the same, except in the case of the +140 mesh fraction, regardless of whether the 50 per cent by weight particle size or the amount of material in the various size fractions were used in attempting to characterize particle size. However, the 50 per cent method produced a single value for each injection and is therefore used in most discussions.

Computer results of the individual sorbents are as follows:

1683 - Twenty-six runs with the aragonite 1683 showed that low mean particle size can be significantly related to SO_2 removal. Within the limits of experimental error the two parameter model using stoichiometry and particle size was able to explain 76 per cent of the variation in SO_2 reactivity for 1683.

1684 - No correlation was seen between SO_2 removal and particle size.

1337 - No correlation was seen between SO_2 removal and particle size.

1359 - The data suggests that the larger 50 per cent sizes had greatest SO_2 removal.

Effect of Injection Temperature

Each of the sorbents, except red mud, was injected at temperatures from 1800°F to 2450°F. Graphical analysis suggests that sample 1683, an aragonite, and 1684, a dolomite, gave best results at 2450°F. Sample 1359, a calcite, performed best at 1800°F with SO_2 removal decreasing as temperature increased. Temperature appeared to have little effect on sample 2077, a chalk, between 1900°F and 2500°F. Also the tests with sample 1337 did not clearly indicate a specific effect of temperature on SO_2 removal. The results are indicated in Appendix A, Figures A-7 through A-11.

The step-wise regression analysis made on the results of 59 runs from samples 1337, 1359, 1683 and 1684 combined, indicated no correlation between the injection temperature and SO_2 removal over the range of test conditions examined.

Computer results on individual sorbents indicated that no significant correlation could be seen between SO_2 removal and injection temperature with samples 1683, 1337 and 1684. However, sample 1359 indicated that lowering the injection temperature within the range examined will lead to increased SO_2 removal.

Effect of Injection Air Velocity

As previously discussed, the injection air volume was controlled in most tests at 640 SCFH. The resulting velocity at this flow rate was 276 feet per second and the calculated Reynolds number within the furnace was 24,286. To further check effects of injection air velocity, stoichiometric amounts (30 pounds per hour)

of -100 mesh sample 1337 were injected at various injection air flow rates from 477 to 716 standard cubic feet per hour. These air flow rates produced injection velocities from 212 to 318 feet per second. Furnace gas stream velocity during these tests was 17.6 feet per second and the calculated Reynolds number of the stream was 18,830. SO_2 removal increased as the velocity was increased as shown in Figure 10. This limited data indicates that the relatively high injection velocity and large Reynolds number significantly increases SO_2 removal rates.

Coal-Limestone Mixture

Sample 1683 was mixed with Number 11 Western Kentucky coal for three runs. Data from the runs are presented in Table III. Results indicate that mixing additive with coal prior to burning on a moving grate is ineffective. Only 10 per cent of the SO_2 was removed at the stone feed rate of 300 pounds per ton of coal (153 per cent of stoichiometric), and only 20 per cent was removed by feeding an unusually large amount, 857 pounds per ton of coal or 437 per cent of stoichiometric. Ash and coal analyses from these runs are listed in Appendix B, page B-3.

TABLE III

COAL - SAMPLE 1683 MIXTURE TESTS

Run No.	#11 Western Ky. Coal Feed Lbs/Hr	Sorbent Feed Lbs/Hr	Sorbent Size	% Stoic. CaO/S	% SO_2 Reduction
58	202	86.5	-28 Mesh	437	20.3
59	192	34.0	-140 +200	180	16.0
62	240	36.0	-28 Mesh	153	9.8

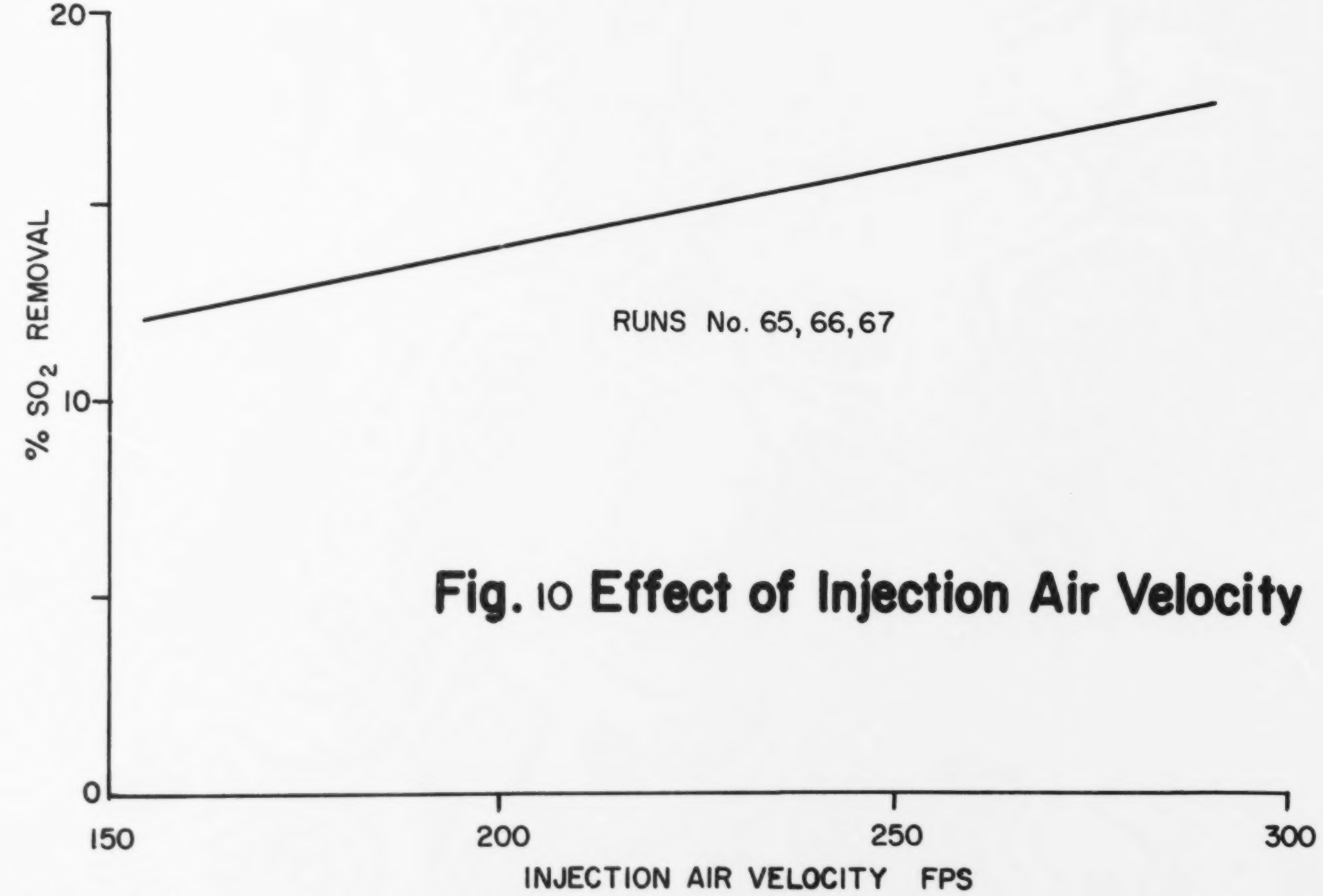


Fig. 10 Effect of Injection Air Velocity

Sulfur Balance

Beginning with run 22, eleven samples were sent to Commercial Testing and Engineering for tests. An evaluation of these samples for sulfur balances (see Appendix A, page A-17) was quite discouraging. In order to compare analytical methods with ASTM C-25-27, NAPCA, TVA, and BCR were asked to supply alternate analytical methods or, in some cases, to run samples of the collected material. The TVA and BCR methods determine per cent sulfur and the ASTM C-25-67 and NAPCA methods determine per cent SO_3. The results of these analyses are shown in Table IV. The agreement between them eliminates the possibility of analytical error. Obviously there were other factors that had been overlooked. Inspection showed that the reacted particulate samples were diluted by flyash and contained a predominance of fine injected particulate. Dilution was determined by making a calcium balance over the system. The absence of larger particles was the result of a poor sample probe design and the inability to sample isokinetically. Therefore, it can be seen from the sulfur balance data that in most cases injections of the finer particles produced the best sulfur balances.

All data in Appendix A, page A-17, starting with run 33 have been corrected for flyash dilution by means of a calcium oxide balance. A sample sulfur balance calculation is shown in Appendix A, page A-19. It is interesting to note that the sulfate form of sulfur was the only form of sulfur found in significant quantities.

TABLE IV

REACTED MATERIAL SULFUR ANALYSES*

Run	NAPCA %S	TVA %S	CT&E C-25-67 Method %S	CT&E BCR Method %S
24	7.80	7.58	7.58	7.75
26	5.34	5.36	5.30	5.36
27	4.70	4.58	4.58	4.58
31	5.45	5.94	5.78	5.75

*See Appendix C, page C-4 for further information on procedures.

An evaluation of the data in Appendix A, page A-17 shows some "as received" materials as producing a sulfur balance. This is probably because of a high fraction of -200 mesh particles present. The use of the calcium balance to determine sample dilution produced a large number of results with a balance of 80 per cent or better. The differences can be attributed to the lack of representative particulate samples from the flue gas stream.

Even though particulate sampling restricted our ability to make good sulfur balances, the writers feel that the data derived from the infrared analyses of the stack gases are more important to this report.

Calcination Levels

Complete data were obtained from 43 tests to perform a statistical analysis of the effects of temperature and particle size on calcination. Loss on ignition of the raw or unreacted sorbent was assumed to be CO_2. Per cent calcination was calculated as follows:

$$\% \text{ Calcination} = 100 - \left(\frac{\% \ CO_2 \text{ in reacted sample}}{\% \ CO_2 \text{ in unreacted sample}} \right) \times 100$$

The data are presented in Appendix A, page A-17, and the results of the least squares fit calculation are shown in Figure 11. Calcination varies directly with temperature between 1700°F and 2500°F. Particle size does not appear to substantially affect calcination. Per cent calcination ranged from 50 to 60 per cent at 1700°F injection temperature and 1.0 to 1.3 seconds residence time to greater than 90 per cent at 2400°F injection temperature and 0.3 to 0.6 seconds residence time. Only small differences are seen in the calcination levels of any of the five injected sorbents at a given temperature level.

When the calcination data for 38 runs of 1337, 1359, 1683 and 1684 were correlated to the independent variables, it was found that 74 per cent of the variation in the degree of calcination could be explained by changes in the injection temperature. The results confirm that particle size of the injected material is apparently not important to the degree of calcination for the conditions employed in this study.

The correlation coefficient between SO_2 removal and degree of calcination was only +0.031. This coefficient indicates that sufficient calcination must have occurred at all of the conditions that were employed to permit SO_2 reaction to proceed. If SO_2 reaction were limited in any way by thedegree of calcination or the rate of calcination, we would expect a stronger correlation between the degree of calcination and SO_2 removal.

A negative correlation coefficient resulted between stoichiometry and the degree of calcination indicating that even though increased stoichiometry leads to increased SO_2 removal, the higher solids loading at high stoichiometric feed rates limits the heat transfer to individual particles. There is then a trade-off

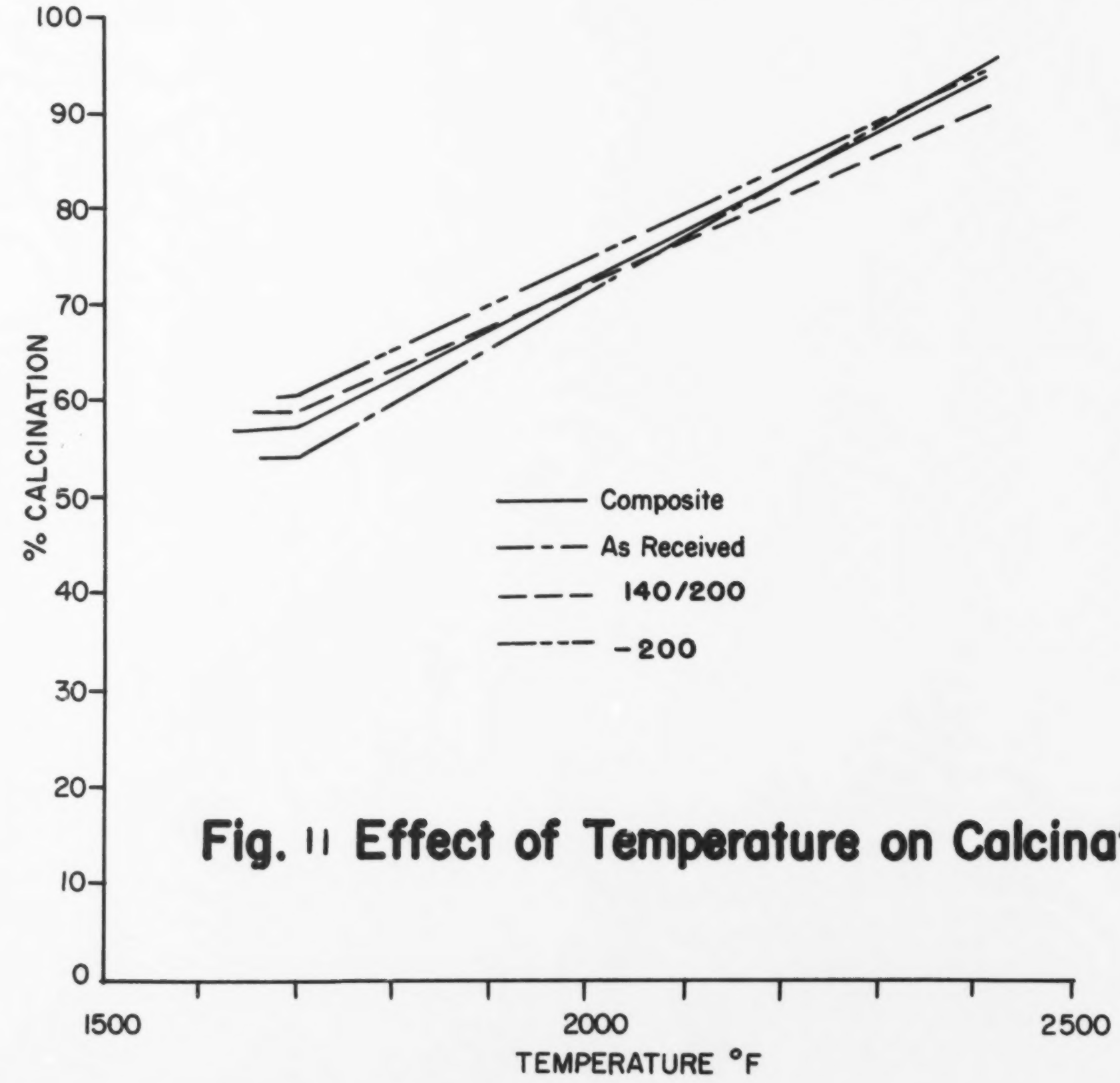


Fig. 11 Effect of Temperature on Calcination

between high calcination and high sorbents feed rates. The same trade-off is observed in calcium oxide utilization and in sorbent efficiency. Apparently the "law of diminishing returns" is important in the limestone injection process. More SO_2 is removed but the individual contribution of a unit weight of material is less.

For sample 1683, 1337, 1684 and 1359 the correlation coefficients relating injection temperature and degree of calcination were +0.77, +0.87, +0.96 and +0.87 respectively. The conclusion on the importance of injection temperature is the same for the individual samples as for the results of all samples combined.

Calcium Oxide Utilization and Additive Efficiency

For the purpose of this report, calcium oxide utilization is expressed by the following formula:

$$\text{CaO Utilization} = \frac{\text{CaO (As } CaSO_4\text{*)} \ \text{(Wt\%)}}{\text{Input CaO (Wt\%)}}$$

(*Measured sulfur removed assumed to be reacted to the sulfate form.)

Calcium oxide utilization varied substantially among the five sorbents tested, and the graphical data did not indicate that any categorical conclusions can be drawn as to whether high or low calcium sorbents yield the best calcium oxide utilization.

Calcium oxide utilization ranged from 6.3 per cent for particle sizes greater than 100 mesh to 59.5 per cent for -200 mesh sizes (see Appendix A, page A-17). Sample 1683 (high calcium aragonite stone) and sample 1684 (low calcium dolomite) indicated best CaO utilization.

The sorbents were compared according to pounds of sulfur removed per pound of sorbent input. The term "sorbent efficiency" has been selected to indicate the values and may be defined as follows:

$$\text{Sorbent Efficiency} = \frac{\text{Sulfur Removed (lbs/unit time)}}{\text{Sorbent Input (lbs/unit time)}} \times 100$$

Results are shown in Appendix A, page A-17. Generally, the high calcium sorbents indicate best efficiency.

When the results of 38 runs on samples 1337, 1359, 1683 and 1684 were combined into a single case, it was found that the stoichiometry and the calcium oxide content are the only independent variables that are significantly related to CaO utilization. Increasing the stoichiometry leads to decreased utilization. Apparently, as in the case of calcination, there is a trade-off between increased SO_2 removal that accompanies increased stoichiometric feed rate and decreased efficiency of utilization of individual particles. The significant negative correlation coefficient between CaO content and utilization suggests that the dolomites are able to achieve higher utilizations than calcites. This hypothesis was confirmed with a t-test which compared the average calcium utilization for calcitic 1359 and 1683 against the average utilization for dolomites 1337 and 1684. Both the t-test and the simple correlation coefficients suggest dolomites achieve higher utilizations than calcites. As would be expected, there was a strong correlation between sorbent efficiency and calcium oxide utilization.

Step-wise regression analysis gave a two parameter model containing stoichiometry and particle size. The model explained 42 per cent of the variation in utilization. Since this is a relatively small amount, we might hypothesize that the sampling problems led to increased uncertainty in the analysis of the utilization data.

For each of the four individual sorbents, 1337, 1359, 1683 and 1684, an increase in efficiency led to a significant increase in utilization. The effect of

particle size varied with the individual sorbents. This accounts for the fact that no significant simple correlation coefficient was obtained for the relationship between particle size and utilization when the data for all of the sorbents were combined.

As in the case of calcium oxide utilization, sorbent efficiency was found to be dependent upon the calcium oxide content and the stoichiometric feed rate. In this case, however, increased CaO was related to increased sorbent efficiency, suggesting that calcites removed more SO_2 per ton of raw stone than do dolomites. When the higher mean value for sorbent efficiency of calcites 1359 and 1683 was compared to the mean sorbent efficiencies for the dolomites 1337 and 1684, a t-test showed the difference between their mean values was significant.

With the exception of 1684, all individual samples had significant correlations between particle size and sorbent efficiency. Samples 1359 and 1337 had higher efficiencies for larger particles whereas sample 1683 had higher efficiency for the smaller particles. The effect of particle size requires further study or improved sampling methods in order to determine how the independent variables affect the sorbent efficiency.

Red Mud Injections

These injection tests were made at the request of NAPCA to verify previous studies made at the Chicago Heating Plant.[7] The sorbent was collected from settling ponds in the St. Louis area,[10] dried, and crushed, and shipped in fiberboard barrels. The handling characteristics of the material were similar to those of clay. Mechanical agglomeration and absorbed moisture caused feeder lines to plug and reduced dispersion patterns necessary for good SO_2 adsorption.

The 1000°F required for injection was not practical in our furnace, and injections

were made at temperatures of 1240°F to 1280°F with sample point temperature at 830°F to 840°F. The sorbent could then pass through the 1000°F range specified for good sorption. Table V summarizes the data collected during the test runs and clearly points out that removal rates were below the average SO_2 sorption rates exhibited by the other materials used in this test. Table VI indicates the chemical analysis of the red mud.

TABLE V

RED MUD TEST DATA

Run Numbers*	48	50	51	54	55	56	57
Carbon Dioxide	5.5	6.0	5.0	7.5	7.5	6.5	6.5
Feed Rate (#/Ton Coal Feed)	218	227	151	200	300	100	150
Injection (Temp. °F)	1240	1280	1280	2050	2100	1930	1950
Sample Pt. (Temp. °F)	840	850	830	1350	1500	1275	1280
SO_2 ppm before injection	1050	1000	1000	1350	1350	1262	1262
SO_2 ppm during injection	875	750	800	1200	1200	1160	1160
SO_2 Removal %	16.7	25.0	20.0	11.1	11.1	8.1	8.1

*Runs numbered 47, 49 were discarded because of unstable furnace conditions.

TABLE VI

CHEMICAL ANALYSIS OF RED MUD

	% Weight Ignited Basis
Phosphorous Pentoxide (P_2O_5)	0.41
Silica (SiO_2)	8.78
Ferric Oxide (Fe_2O_3)	33.87
Alumina (Al_2O_3)	18.40
Titania (TiO_2)	14.44
Lime (CaO)	14.16
Magnesia (MgO)	1.35
Sulfur Trioxide (SO_3)	3.20
Sodium Oxide (Na_2O)	5.00
Undetermined	0.48
	100.00

APPENDIX A

TEST RUN DATA

TEST DATA

Run No.	Sample No.	Coal Feed Rate #/Hr	Sorbent Feed Rate #/Ton Coal	Injection Temp. °F	Sorbent Size (Screen Cut)	CaO/S Stoic. %	Excess Air %	SO_2 Reduction %
1	1683	300	220	----	-140/200	114	70	56.7
2	"	V O I D						
3	"	300	247	----	-140/200	128	70	51.7
4	"	300	100	----	-140/200	52	60	20.0
5	"	300	100	2100	-200	67	100	17.9
6	"	V O I D		SAMPLE PUMP FAILURE				
7	"	300	100	2260	As Rec.	49	80	9.8
8	"	300	200	2260	As Rec.	98	80	22.6
9	"	300	300	2250	As Rec.	147	80	32.3
10	"	300	100	2280	-200	49	80	21.9
11	"	300	200	2280	-200	98	80	50.0
12	"	300	300	2260	-200	147	80	65.6
13	"	156	192	1800	-140/200	94	90	36.2
14	"	156	384	1810	-140/200	189	90	62.1
15	"	156	141	1820	As Rec.	69	90	17.2
16	"	156	192	1800	As Rec.	94	90	20.7
17	"	156	282	1800	As Rec.	138	90	27.6
18	"	156	90	1850	-140/200	44	100	10.7
19	"	156	192	1850	-140/200	94	100	25.0
20	"	300	200	2100	As Rec.	98	90	16.7
21	"	300	300	2100	As Rec.	147	100	23.2
22	"	300	200	2100	-140/200	98	90	48.3
23	"	300	200	2200	As Rec.	98	90	23.3
30	"	500	200	2380	-140/200	99	35	42.7
31	"	500	200	2440	-200	99	35	58.5
61	"	300	200	1600	As Rec.	98	80	10.9

TEST DATA - CONT'D

Run No.	Sample No.	Coal Feed Rate #/Hr	Sorbent Feed Rate #/Ton Coal	Injection Temp. °F	Sorbent Size (Screen Cut)	CaO/S Stoic. %	Excess Air %	SO_2 Reduction %
76	1683	348	190	2480	As Rec.	96	30	5.9
77	"	348	190	2440	-140/200	96	35	24.1
78	"	348	190	2450	-200	96	35	32.1
88	"	323*	279	1800	As Rec.	102	85	9.7
89	"	300	200	2170	-200	101	50	41.8
90	"	300	300	2175	-200	151	35	54.5
91	"	274	146	1930	-200	73	130	14.9
24	1337	300	93	2200	As Rec.	25	60	19.4
25	"	300	173	2200	As Rec.	47	60	36.1
26	"	300	173	2060	-140/200	47	95	36.8
27	"	300	557	2100	As Rec.	151	105	77.8
32	"	200	380	1880	As Rec.	104	105	46.3
35	"	300	380	1850	-200	103	60	24.1
38	"	165	310	1775	As Rec.	102	90	36.7
41	"	185	378	1780	-140/200	118	110	42.3
44	"	185	378	1800	-200	118	90	24.1
52	"	300	VOID					
53	"	300	347	2060	As Rec.	100	80	12.9
60	"		VOID					
63	"	275	200	2100	As Rec.	59	70	14.2
64	"	275	200	2100	As Rec.	59	70	11.1
65	"	275	200	2100	As Rec.	59	60	13.4
66	"	275	200	2300	As Rec.	59	60	14.4

*High sulfur coal

TEST DATA - CONT'D

Run No.	Sample No.	Coal Feed Rate #/Hr	Sorbent Feed Rate #/Ton Coal	Injection Temp. °F	Sorbent Size (Screen Cut)	CaO/S Stoic. %	Excess Air %	SO_2 Reduction %
67	1337	275	200	2300	As Rec.	59	60	16.9
68	"	275	VOID					
79	"	348	339	2450	As Rec.	95	85	27.4
80	"	348	339	2500	-140/200	95	85	31.6
81	"	348	339	2450	-200	95	10	30.1
28	1359	300	257	2120	-140/200	135	110	42.3
34	"	300	260	2300	As Rec.	127	80	30.6
37	"	300	260	2175	-200	127	80	26.6
39	"	165	254	1775	As Rec.	124	110	40.4
43	"	185	265	1800	-140/200	129	105	47.2
46	"	185	270	1770	-200	132	95	29.8
82	"	348	190	2450	As Rec.	95	35	21.6
83	"	348	190	2480	-140/200	95	10	25.5
84	"	348	190	2450	-200	95	60	27.4
92	"	323*	279	2100	As Rec.	102	100	23.5
93	"	323*	279	2080	-200	102	100	23.5
94	"	323*	279	2000	-200	102	130	25.1
29	1684	300	407	2060	-140/200	111	115	59.2
33	"	300	420	2250	As Rec.	115	100	39.3
36	"	300	420	2200	-200	115	95	24.6
40	"	300	411	1780	As Rec.	115	105	29.6
42	"	185	411	1800	-140/200	118	105	34.0
45	"	185	411	1780	-200	115	90	27.6

*High sulfur coal

TEST DATA - CONT'D

Run No.	Sample No.	Coal Feed Rate #/Hr	Sorbent Feed Rate #/Ton Coal	Injection Temp. °F	Sorbent Size (Screen Cut)	CaO/S Stoic. %	Excess Air %	SO_2 Reduction %
85	1684	348	339	2420	As Rec.	95	35	38.0
86	"	348	339	2420	-140/200	95	60	40.0
87	"	348	339	2420	-200	95	35	47.0
69	2077	274	219	1900	As Rec.	93	75	17.7
70	"	274	219	2000	As Rec.	93	65	21.1
71	"	274	219	2000	-100	93	85	22.6
72	"	168	238	1700	As Rec.	101	100	22.0
73	"	168	238	1800	-100	101	120	31.4
74	"	348	230	2450	-100	98	55	30.3
75	"	348	230	2400	As Rec.	98	55	20.6

TABLE A-2

SCREEN SIZE DATA

Run No.	Material	Screen Cut	% SO_2 Removal	Temp. °F	Weight % Passing Indicated Mesh Size				
					50	100	140	200	325
36	1684	-200	20.0	2200	100.0	91.2	73.2	31.2	6.0
40	"	As Rec.	24.5	1780	92.4	71.6	46.0	26.0	7.6
42	"	140/200	28.2	1800	99.6	99.2	93.2	17.2	5.2
45	"	-200	22.9	1780	100.0	99.2	89.6	54.4	16.8
85	"	As Rec.	39.9	2420	93.1	81.7	54.2	24.5	5.9
86	"	140/200	42.0	2420	99.6	99.2	90.7	16.1	4.0
87	"	-200	49.4	2420	100.0	98.9	94.9	76.7	31.6
37	1359	-200	19.5	2175	100.0	90.4	60.8	38.4	12.0
39	"	As Rec.	30.3	1775	98.4	89.2	72.0	50.8	20.8
43	"	140/200	34.0	1800	100.0	88.0	54.4	16.0	1.6
46	"	-200	21.0	1770	100.0	99.3	93.7	63.5	25.4
82	"	As Rec.	22.7	2450	99.3	92.8	74.2	48.8	25.4
83	"	140/200	26.8	2480	97.3	89.2	70.3	50.0	24.3
84	"	-200	28.8	2450	100.0	98.8	96.4	79.2	46.4
92	"	As Rec.	23.0	2100	99.1	93.0	74.4	50.3	19.7
93	"	-200	23.0	2080	100.0	99.6	98.4	84.8	56.4
35	1337	-200	21.6	1850	100.0	99.6	95.2	65.6	16.8
38	"	As Rec.	33.3	1775	99.6	80.4	51.6	27.2	8.0
41	"	140/200	38.1	1780	0	100.0	73.6	20.4	4.8
44	"	-200	21.7	1880	0	100.0	99.2	56.0	14.8
79	"	As Rec.	28.8	2450	99.6	77.2	50.4	28.0	8.8
80	"	140/200	33.2	2500	100.0	99.6	84.7	27.0	5.7
81	"	-200	31.6	2450	0	100.0	99.2	71.5	16.5

TABLE A-2 (Cont'd)

Run No.	Material	Screen Cut	% SO_2 Removal	Temp. °F	Weight % Passing Indicated Mesh Size				
					50	100	140	200	325
70	2077	As Rec.	22.7	2200	46.6	7.3	4.8	2.8	0.8
71	"	Pulverized	24.3	2000	93.7	71.3	46.1	27.6	14.2
72	"	As Rec.	21.9	1700	54.0	15.8	8.9	6.1	2.4
73	"	Pulverized	31.4	1800	99.6	98.1	75.7	63.9	44.5
74	"	Pulverized	30.8	2450	98.0	87.0	78.8	65.5	50.6
75	"	As Rec.	21.0	2400	66.4	44.0	31.2	20.4	10.0
76	1683	As Rec.	6.1	2480	42.4	15.9	6.9	1.6	0.4
77	"	140/200	34.1	2440	99.6	90.0	55.6	21.6	6.0
78	"	-200	46.3	2450	100.0	99.2	96.4	86.3	54.3
88	"	As Rec.	9.6	1800	59.6	28.4	13.6	3.2	0.8
89	"	-200	41.7	2170	99.7	98.8	95.7	79.2	41.4
90	"	-200	36.1	2175	100.0	93.6	80.4	56.4	22.8
91	"	-200	20.4	1930	100.0	97.8	89.9	63.3	26.6

SAMPLE 1683

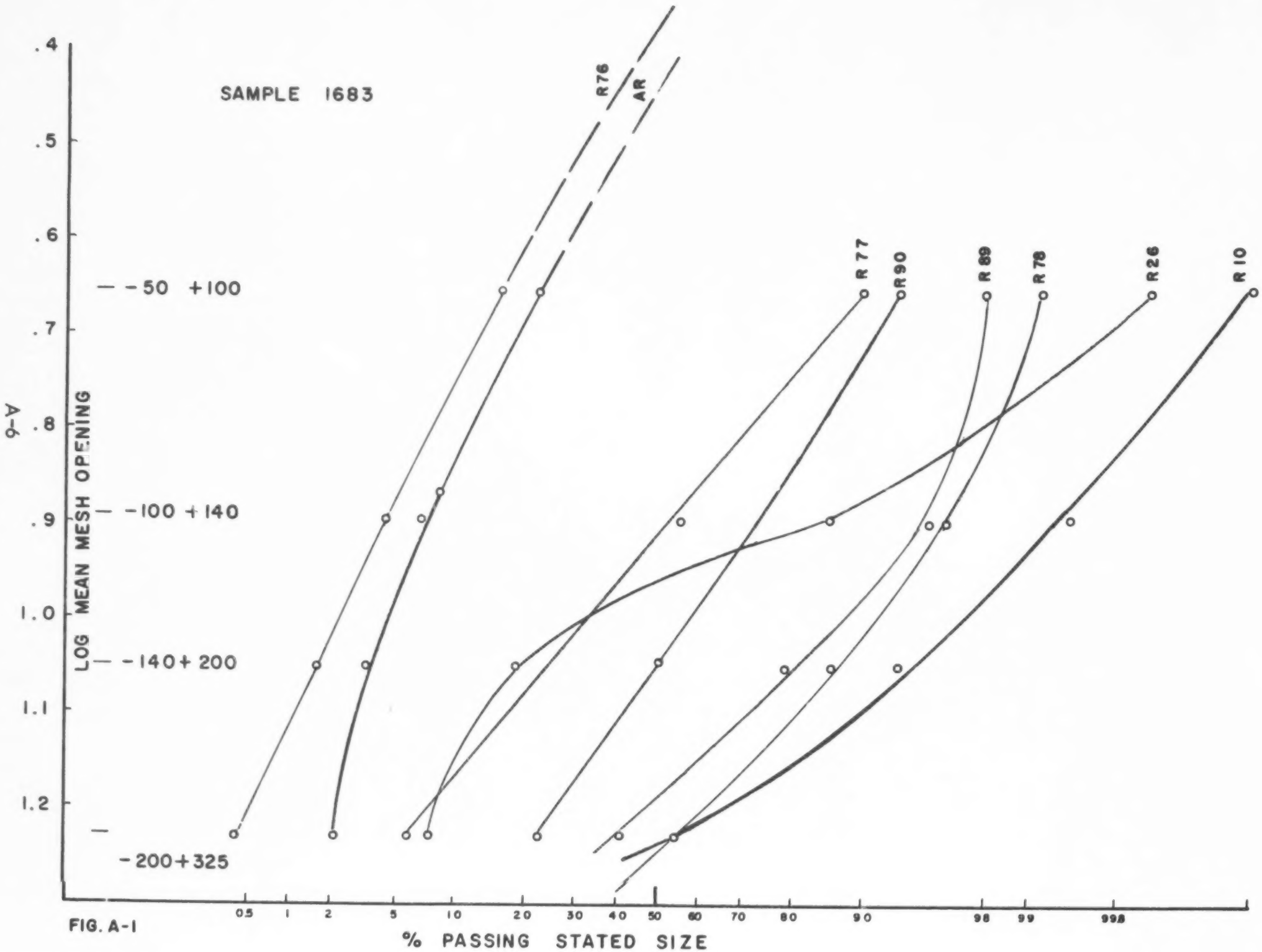


FIG. A-1

SAMPLE 1359

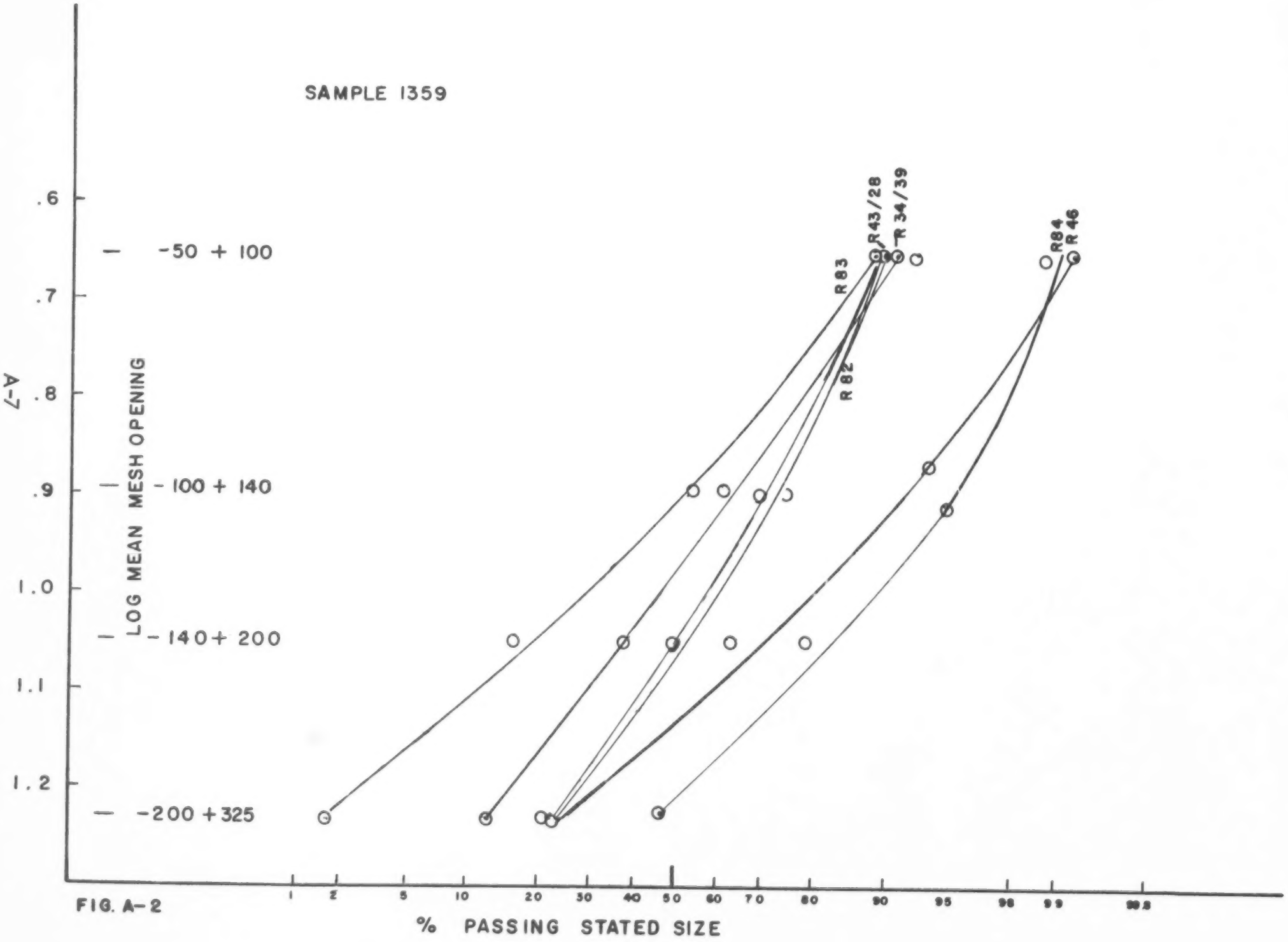


FIG. A-2

SAMPLE 1337

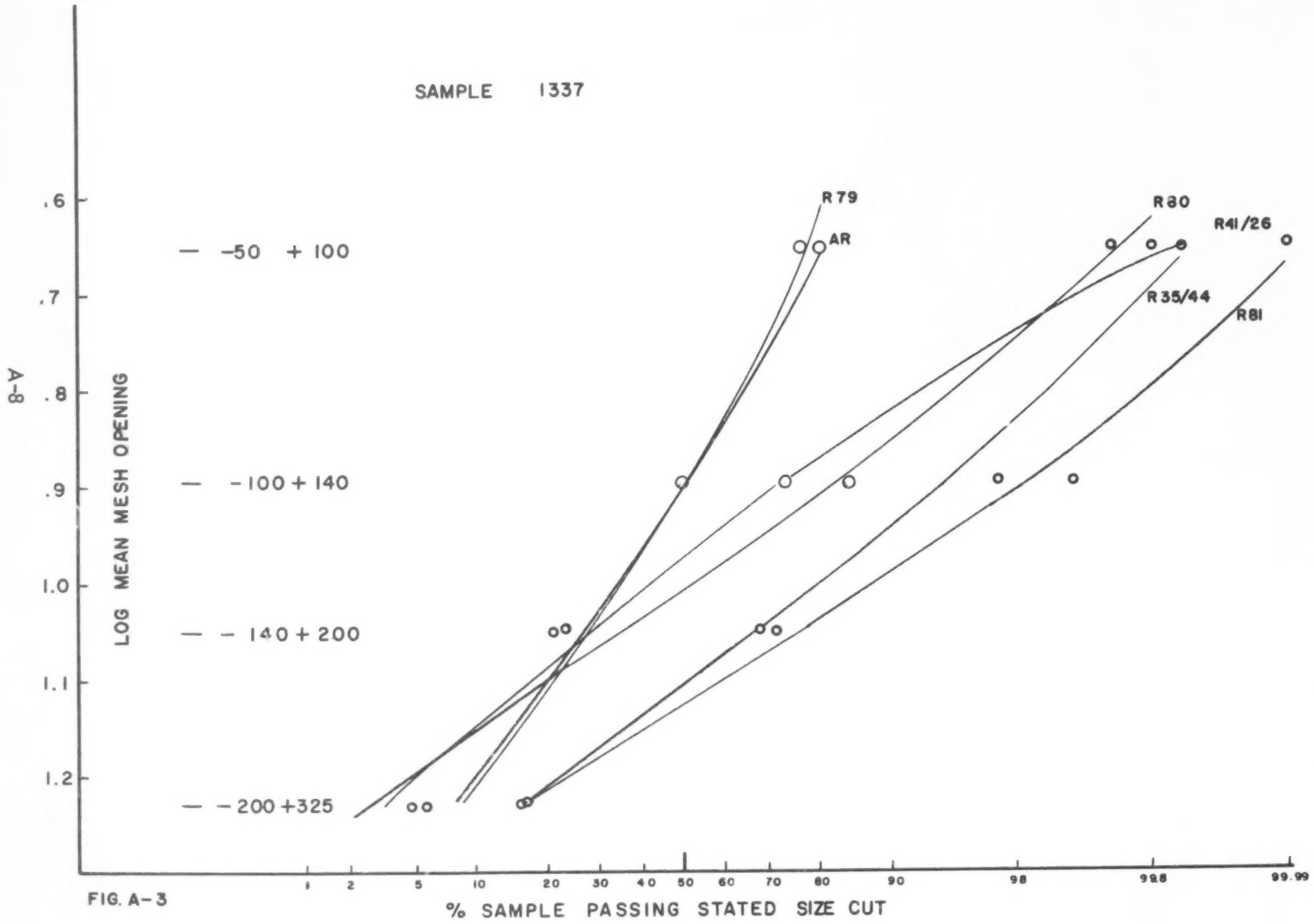


FIG. A-3

SAMPLE 1684

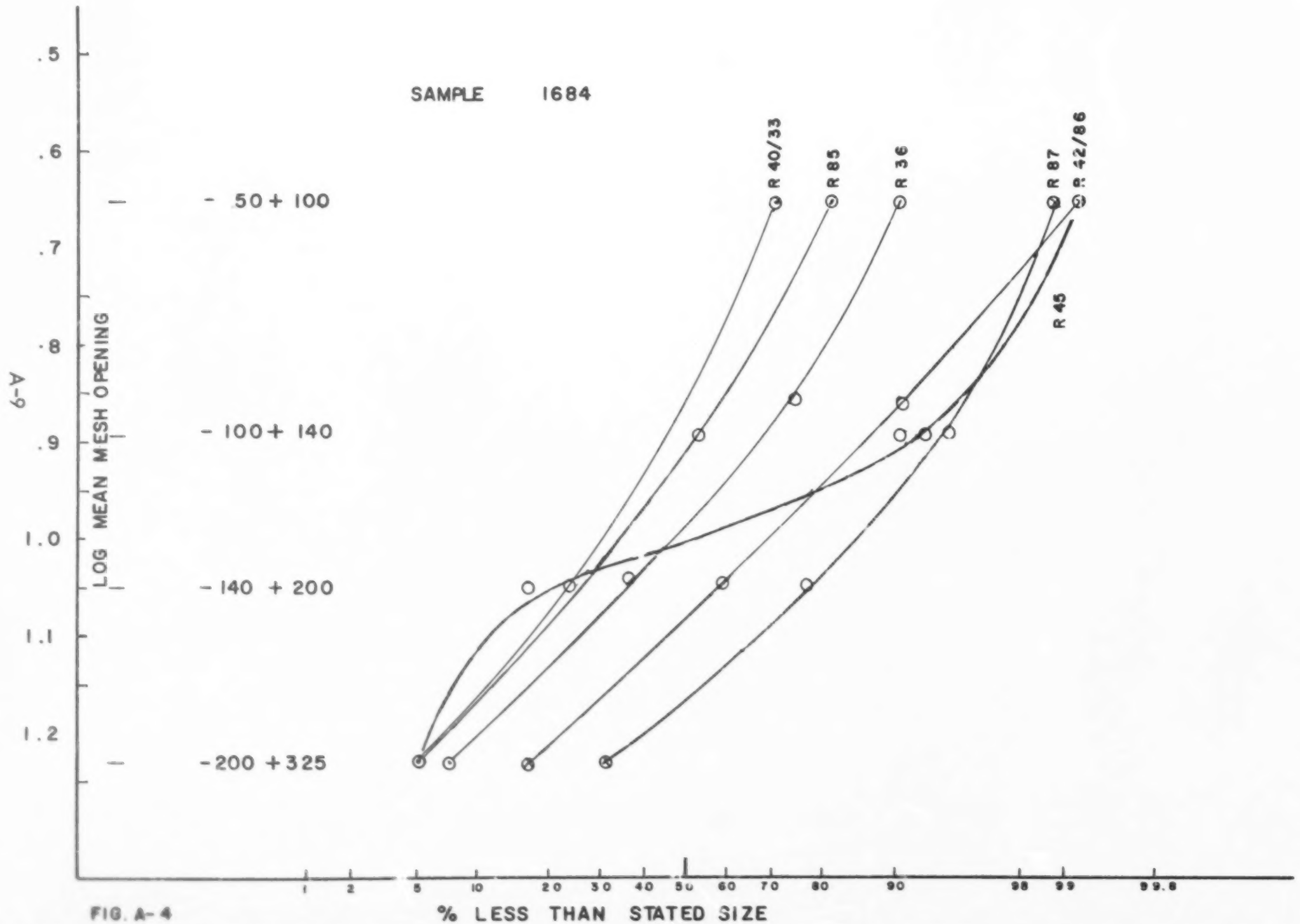


FIG. A-4

SAMPLE 2077

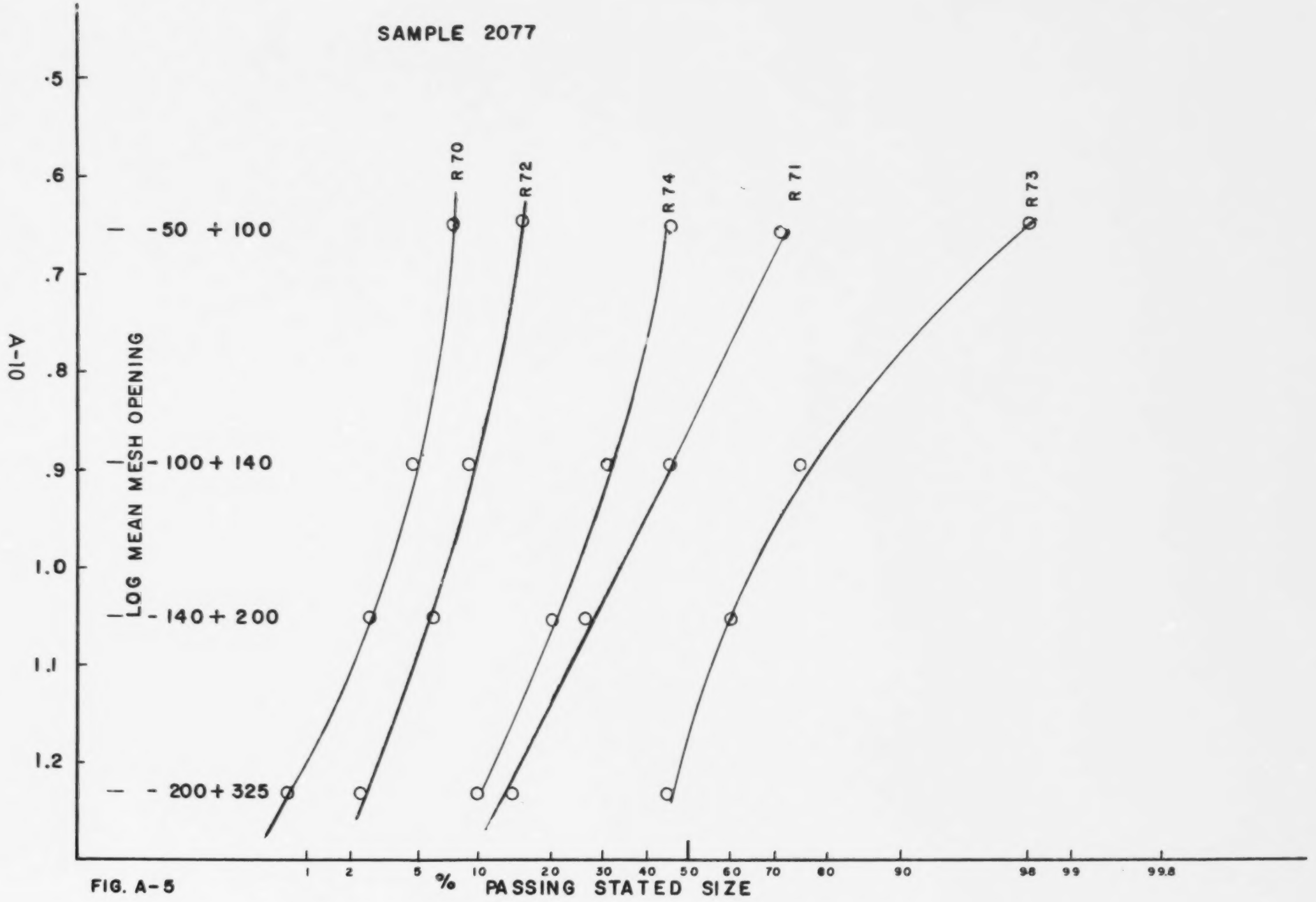


FIG. A-5

SAMPLE 1684

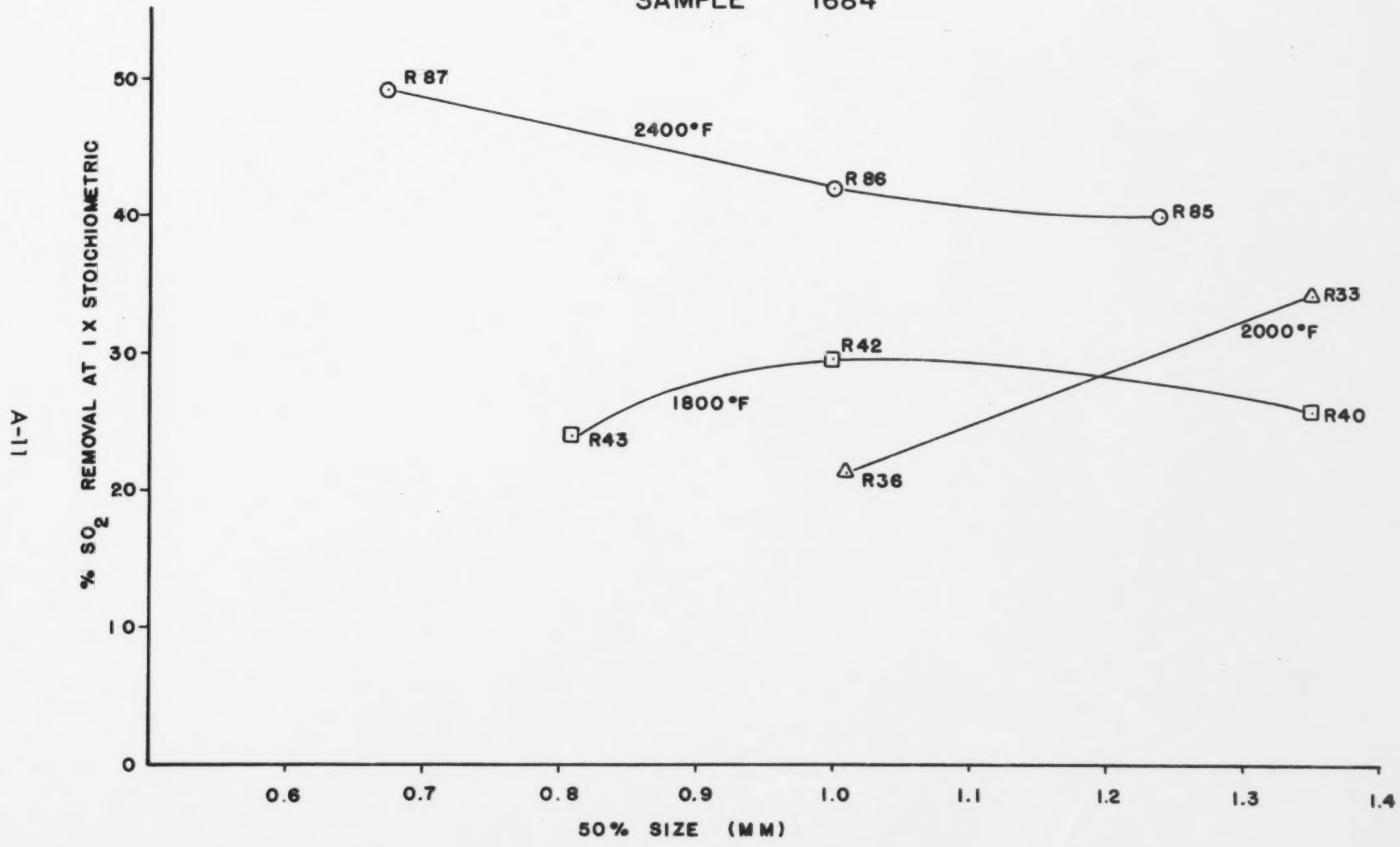
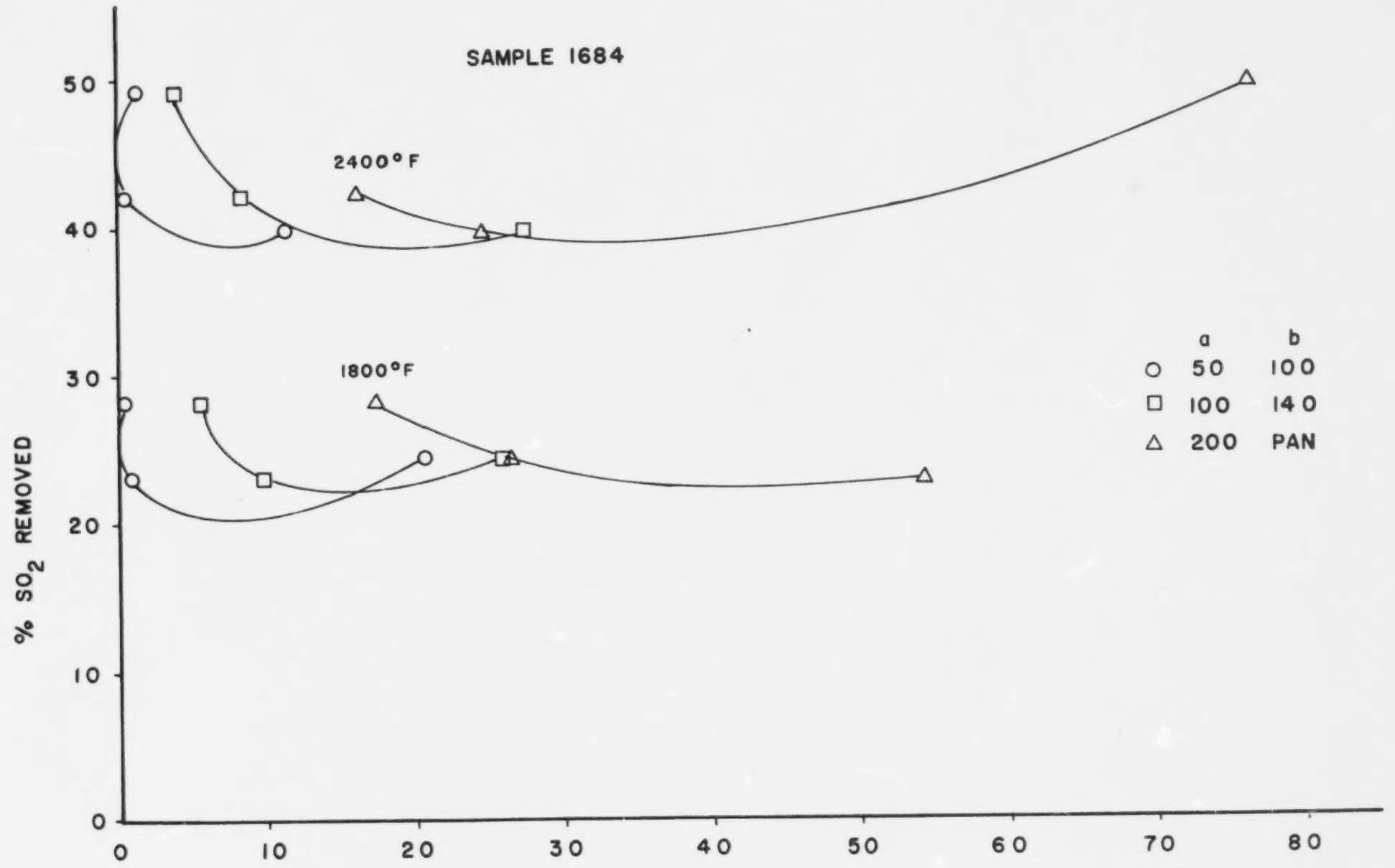


FIGURE A-6



WEIGHT PERCENT PASSING a, RETAINED ON b

FIG. A-7

SAMPLE 1683

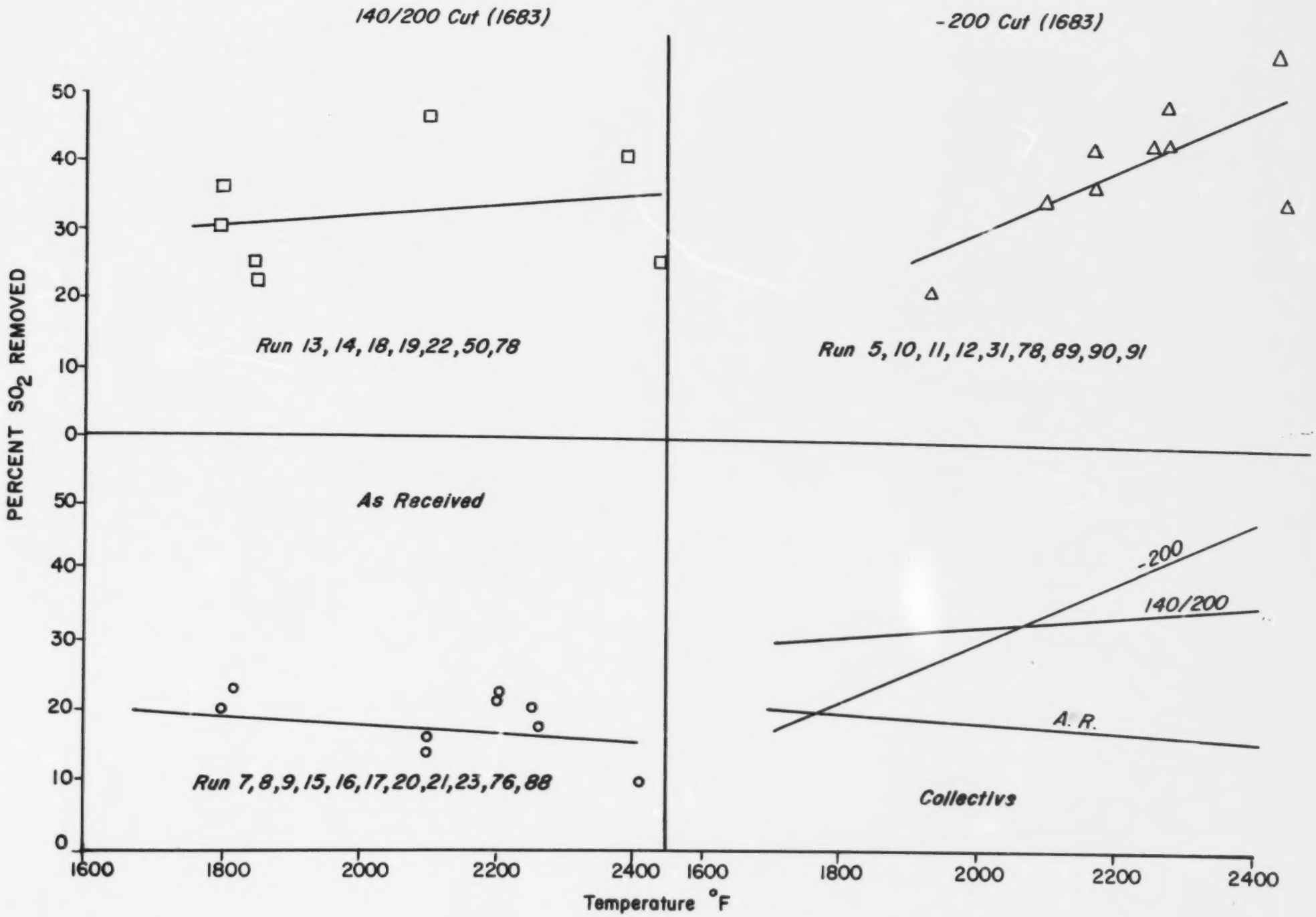


FIG. A-8

SAMPLE 2077

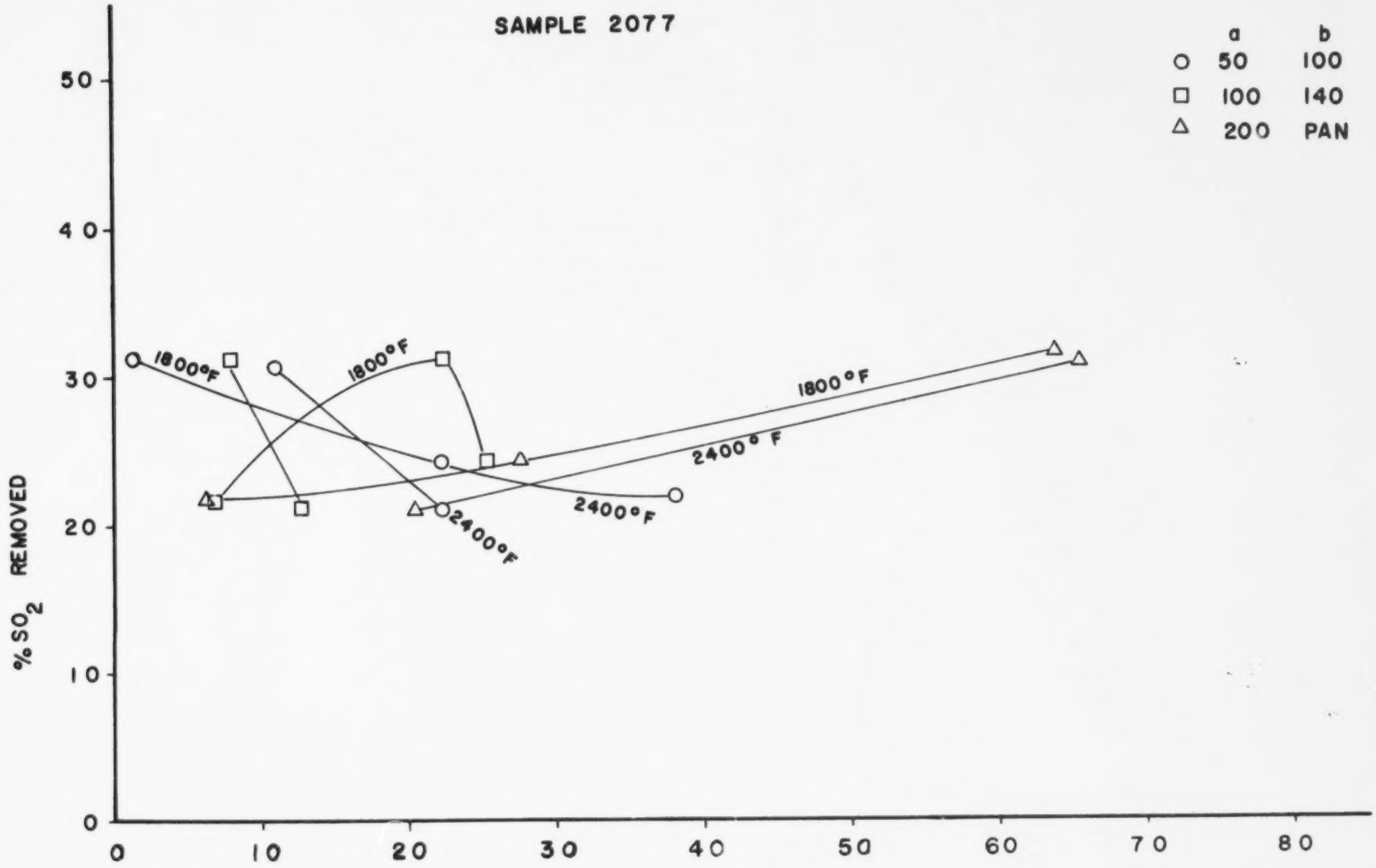
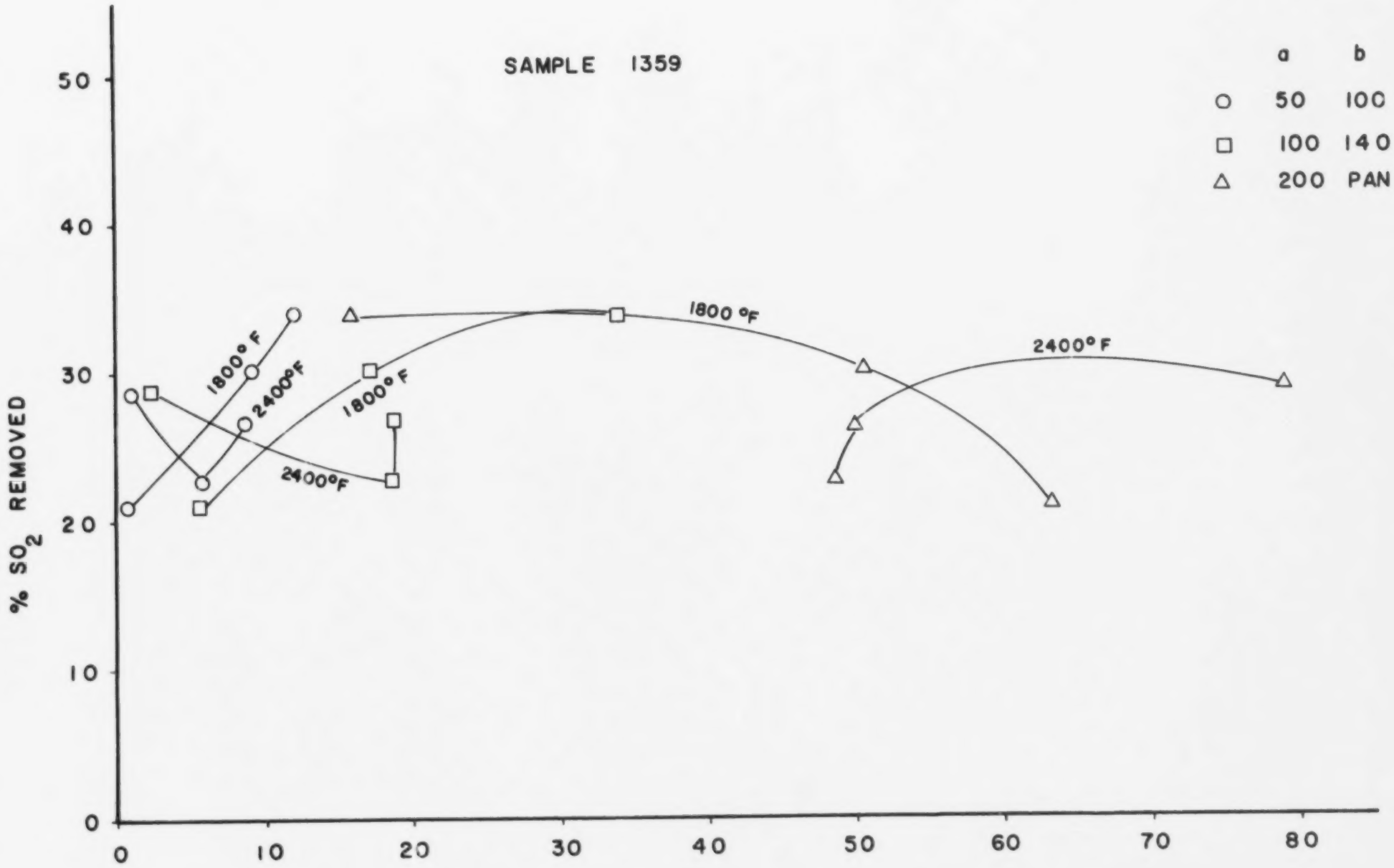


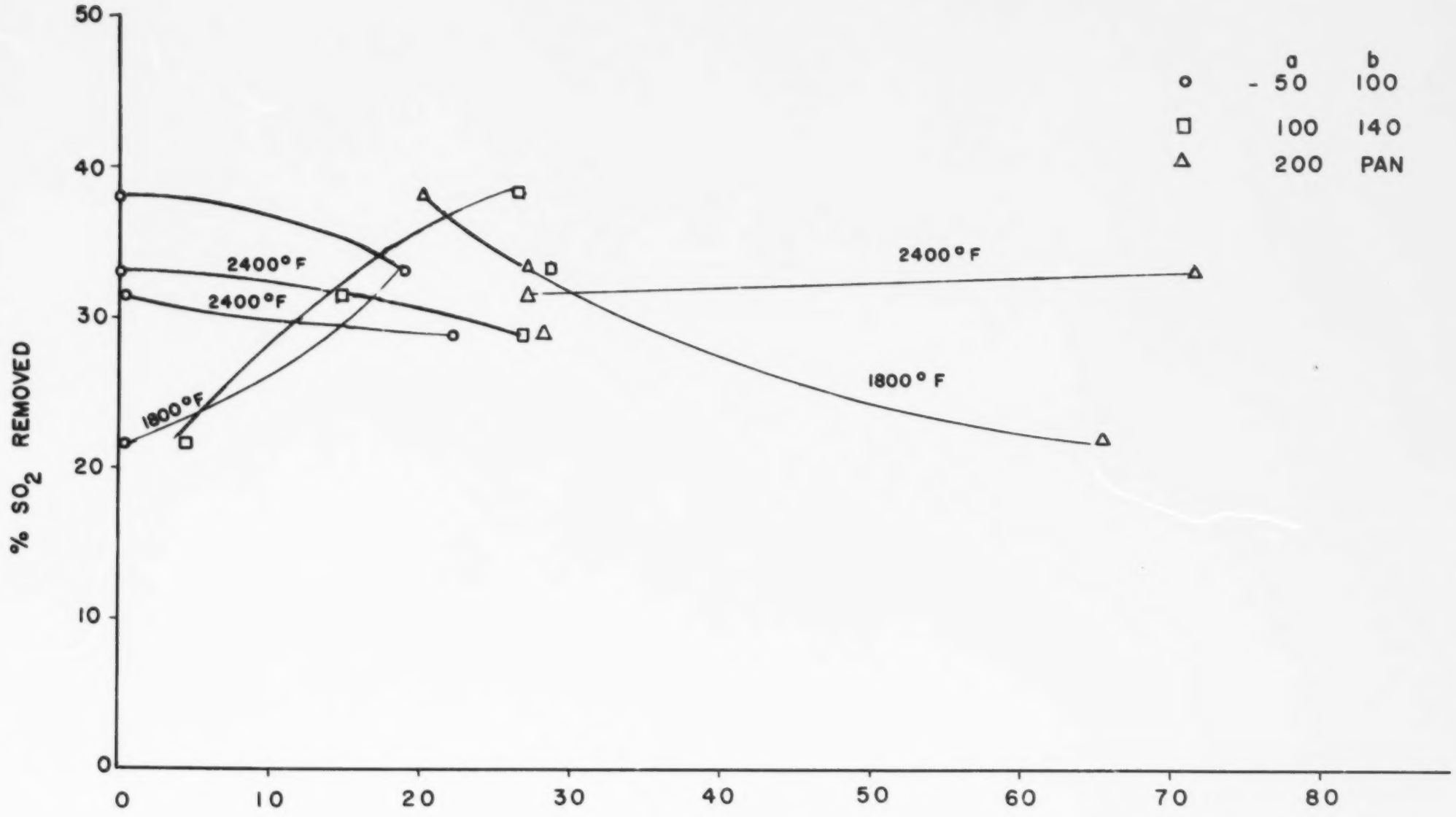
FIG. A-9



WEIGHT PERCENT PASSING a, RETAINED ON b

FIG. A-10

SAMPLE 1337



WEIGHT PERCENT PASSING a, RETAINED ON b

FIG. A-11

TABLE A-3

CALCINATION AND UTILIZATION DATA

Run No.	Sample No.	Sorbent Size	Lbs. Sorbent Ton Coal	Injection Temp. °F	Cal. %	% CaO Util.	% Sorbent Efficiency	% SO_3 Measured	% Sulfur Balance
22	1683	140	200	2100	84.1	49.3	15.1	11.28	33.3
23	1683	A R	200	2200	82.1	23.8	7.3	12.59	64.3
24*	1337	A R	94	2200	92.0	76.6	13.0	17.95	61.6
25*	1337	A R	174	2220	92.2	76.2	13.0	16.74	52.6
26*	1337	140	174	2060	84.9	77.7	13.2	11.33	36.2
27	1337	A R	558	2100	78.3	51.1	8.7	9.01	37.3
28	1359	140	257	2120	85.1	33.9	10.3	12.74	48.3
29	1684	140	407	2060	74.5	54.2	9.2	8.01	32.8
30	1683	140	200	2380	90.1	43.4	13.3	8.36	26.1
31	1683	-200	200	2440	91.9	59.5	18.2	11.47	28.6
33	1684	A R	420	2250	87.1	34.3	5.8	13.59	100.9
34	1359	A R	260	2300	91.2	24.2	7.3	15.31	71.9
35	1337	-200	380	1850	82.9	23.2	4.0	11.74	90.8
36	1684	-200	420	2200	84.1	54.9	3.6	11.25	92.2
37	1359	-200	260	2175	86.0	21.0	6.4	15.27	82.1
38	1337	A R	310	1775	54.8	35.8	6.1	7.50	47.5
39	1359	A R	254	1775	54.1	32.6	9.9	8.54	38.1
40	1684	A R	411	1780	38.9	26.4	4.5	4.67	42.1
41	1337	140	378	1780	58.9	40.9	7.0	9.33	53.2
42	1684	140	411	1800	62.8	30.3	5.2	8.86	63.2
43	1359	140	265	1800	58.4	36.5	11.1	11.66	47.7
44	1337	-200	378	1800	66.1	23.3	4.0	11.37	101.2
45	1684	-200	411	1780	46.1	24.6	4.2	8.71	81.6
46	1359	-200	270	1770	62.9	22.6	6.9	17.32	100.6

*Runs could not be duplicated

TABLE A-3 (Cont'd)

Run No.	Sample No.	Sorbent Size	Lbs. Sorbent Ton Coal	Injection Temp. °F	Cal. %	% CaO Util.	% Sorbent Efficiency	% SO_3 Measured	% Sulfur Balance
69	2077	A R	219	1900	77.8	19.5	5.0	11.20	78.1
70	2077	A R	219	2000	83.1	23.3	6.0	14.35	84.0
71	2077	-325	219	2000	90.2	25.0	6.4	8.32	101.2
72	2077	A R	238	1700	56.8	22.3	5.8	3.09	52.3
73	2077	-325	238	1800	58.1	32.1	8.2	5.58	56.1
74	2077	-325	230	2450	95.4	32.0	8.2	7.95	70.2
75	2077	A R	230	2400	97.6	21.7	5.6	7.17	109.9
76	1683	A R	190	2480	93.2	6.3	1.9	4.87	239.9
77	1683	140	190	2440	95.1	25.9	7.9	3.33	33.5
78	1683	-200	190	2450	96.3	34.5	10.6	8.97	73.5
79	1337	A R	339	2450	95.8	29.7	5.9	7.02	84.4
80	1337	140	339	2500	92.2	34.1	6.5	6.43	70.6
81	1337	-200	339	2450	95.3	32.5	6.4	5.43	73.8
82	1359	A R	190	2450	80.7	23.4	7.1	6.98	103.2
83	1359	140	190	2480	86.5	27.6	8.4	8.58	95.6
84	1359	-200	190	2450	87.4	29.7	9.0	10.75	101.6
85	1684	A R	339	2420	95.9	41.2	8.1	8.26	82.0
86	1684	140	339	2420	95.4	43.2	8.5	8.26	71.9
87	1684	-200	339	2420	98.1	50.8	10.0	11.08	88.6
88	1683	A R	279	1800					
89	1683	-200	200	2170	60.9	42.6	13.9	8.34	57.5
90	1683	-200	300	2175	77.9	37.0	11.3	10.73	87.3
91	1683	-200	146	1930					
92	1359	A R	279	2100	45.7			4.74	67.7
93	1359	-200	279	2080	40.6			4.94	73.9
94	1683	-200	279	2000	27.0			6.63	98.2

SAMPLE CALCULATIONS

Sulfur Balance of Run 82

Coal Results:

348 lbs. coal x 3.38% S/lb. of coal = 11.76 lbs. Sulfur available

0.0719 lbs. ash ultimate analysis = 0.0917 lbs. dry refuse/lb. coal
1-0.2159 lbs. combustable in ash

348 lbs. coal x 0.0917 x 10%* to fly ash = 3.19# flyash

Injected Material:

33 lbs. injected sorbent x 80.71% calcination = 26.63 lbs. sorbent calcined.

33 - 26.63 = 6.37 non-calcined sorbent

26.63 lbs. x 43.37% LOI of sorbent = 11.55 lbs. of gas lost.
26.63 lbs. - 11.55 lbs. = 15.08 lbs. calcined sorbent.

33 lbs. sorbent x 53.19% CaO in sorbent = 17.55 lbs. CaO available

6.37 lbs. uncalcined sorbent x 43.37% LOI = 2.76 lbs. CO_2

17.55 lbs. CaO available = 36.51 total lbs. reacted material
48.07% CaO analyzed by CT&E in reacted sample material

I R Analysis:

11.76 lbs. sulfur available x 21.60% SO_2 reduction = 2.47 lbs. sulfur to sorbent

Material Available to Reacted Sample:

2.47 lbs. Sulfur
15.08 lbs. Calcined Sorbent
6.37 lbs. Non-Calcined Sorbent
3.19 lbs. Flyash estimated
27.11 lbs. Total Material

36.51 lbs. Total material calculated from CT&E
-27.11 lbs. Predicted
9.40 lbs. Dilution

	Predicted	CT&E Results
2.47 lbs. sulfur ÷ 36.51 lbs. x 100 =	6.76% S	6.98% Sulfur
17.55 lbs. CaO ÷ 36.51 lbs. x 100 =	48.07% CaO	48.07% CaO
2.76 lbs. CO_2 ÷ 36.51 lbs. x 100 =	7.56% CO_2	2.76% CO_2

$$\frac{\text{6.98\% Sulfur analyzed} \times 100}{\text{6.76\% Sulfur predicted}} = 103.25\% \text{ Sulfur Balance}$$

*Determined experimentally

APPENDIX B

COAL DATA

TABLE B-1

NUMBER 11 WESTERN KENTUCKY COAL

Average Ultimate Analysis (Dry)

1-1/2" x 28 Mesh Size (Washed)

% C	74.60
% H_2	5.23
% N_2	1.07
% Cl	.04
% Ash	7.31
% O_2 by difference	8.26
% S	3.49
	100.00

% S As Received	3.14
% H_2O (as received)	7.02
Free swelling index	3-1/2

Sulfur Types (% by wt.) Dry

Pyritic	1.29
Sulfate	.05
Organic	2.15
	3.49

Mineral Analysis of Ash (% by wt.) (Ignited Basis)

P_2O_5	1.39
SiO_2	37.20
Fe_2O_3	31.57
Al_2O_3	19.13
TiO_2	1.06
CaO	4.25
MgO	1.17
SO_3	1.82
K_2O	1.95
Na_2O	0.43
Undetermined	0.03
	100.00

Fusion Temperature of Ash

	Reducing
Initial Deformation	1975°F
Softening (H = W)	2155°F
Softening (H = 1/2W)	2245°F
Fluid	2400°F

BTU As Received	12,485
BTU Dry Basis	13,515

TABLE B-2

STONEFORT COAL

SOUTHERN ILLINOIS

1-1/2 x O Size (Unwashed)

Ultimate Analysis (Dry)

% C	63.85
% H_2	4.55
% N_2	0.78
% Cl	0.10
% Ash	20.95
% O_2 by difference	4.96
% S	4.81
	100.00
% S (Wet)	4.47
% H_2O (As Received)	6.97

Sulfur Types (% by wt.) Dry

Pyritic	3.67
Sulfate	.19
Organic	.95
	4.81

Mineral Analysis of Ash (% by wt.) (Ignited Basis)

P_2O_5	0.59
SiO_2	44.30
Fe_2O_3	31.07
Al_2O_3	11.14
TiO_2	0.50
CaO	5.86
MgO	0.83
SO_3	3.73
K_2O	1.67
Na_2O	0.10
Undetermined	0.21
	100.00

Fusion Temperature of Ash

	Reducing	Oxidizing
Initial Deformation	2010°F	2295°F
Softening (H = W)	2045°F	2375°F
Softening H = (1/2W)	2075°F	2440°F
Fluid	2110°F	2550°F

BTU As Received	10,922
BTU Dry Basis	11,740

TABLE B-3

COAL LIMESTONE MIXTURES

Ultimate Analysis (As Rec.) % by wt.	Run #58	#59	#62
H_2O	6.53	8.78	
C	60.33	60.61	
H_2	4.12	4.13	
N_2	0.92	0.92	
Cl	0.04	0.05	
S	2.55	2.56	
Ash	16.93	14.06	
O_2	8.58	8.89	
	100.00	100.00	
Mineral Analysis of Ash % by wt. Ignited Basis			
P_2O_5	0.20	0.38	0.18
SiO_2	13.26	15.85	17.73
Fe_2O_3	9.03	10.54	12.28
Al_2O_3	6.63	8.52	10.09
TiO_2	0.46	0.54	0.48
CaO	53.30	47.13	45.57
MgO	0.91	1.41	0.95
SO_3	14.92	14.52	11.02
K_2O	0.55	0.64	0.68
Na_2O	0.34	0.34	0.30
Undetermined	0.40	0.13	0.72
	100.00	100.00	100.00

SOURCE AND NOMENCLATURE OF INJECTION MATERIALS

Sorbent 1337	Dolite Chas. Pfizer Co. Gibsonburg, Ohio
Sorbent 1359	Grove Lime Grove Lime Co. Stephens City, Virginia
Sorbent 1683	Aragonite Ocean Industries Ft. Lauderdale, Florida
Sorbent 1684	Corson Lime G & WH Corson, Inc. Plymouth Meeting, Pennsylvania
Sorbent 2077	Austin Chalk Kaiser Cement San Antonio, Texas
"RED MUD"	Courtesy of: General Motors, St. Louis, Mo. Republic Coal & Coke, Chicago, Ill.

APPENDIX C

REFERENCES, DEFINITIONS AND LABORATORY IDENTIFICATION

REFERENCES

1. TVA, "Sulfur Oxide Removal From Power Plant Stack Gas." Conceptual Design and Cost Study Prepared for the National Center for Air Pollution Control, 1968.

2. Boynton, Robert S., "Chemistry and Technology of Lime and Limestone." Interscience Publishers, a Division of John Wiley & Sons, Second Printing, February, 1968.

3. Harrington, R. E., Borgwardt, R. H., and Potter, A.E., "Reactivity of Selected Limestones and Dolomites with Sulfur Dioxide." Control Technology Research and Development Program, National Center for Air Pollution Control, Public Health Service, Cincinnati, Ohio.

4. Lewis, W. K., Radasch, A. H., and Lewis, H. C., "Industrial Stoichiometry." Second Edition, McGraw-Hill.

5. Potter, P. J., "Power Plant Theory and Design." Ronald Press.

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7. Linna, E. W., "Trial Usage of Additives Controlling Sulfur Dioxide Emissions From Coal Burning." City of Chicago, Illinois, October, 1968.

8. Kruel, M., and Juntgen, H., "On the Reaction of Calcined Dolomite and Other Alkaline Earth Compounds with the Sulfur Dioxide of Combustion Gases Carried out in Cloud of Suspended Dust." Chemie Ingenieur Technik, May, 1967.

9. Ishihara, Y., Asakawa, C., and Hukuzawa, H., "Pilot Furnace Investigation for Removing Sulfur Dioxide From Combustion Gases with Limestone Injection Method." Research Committee for Air Pollution Control, Central Research Institute of Electric Power Industry, Japan, 1967.

10. Shepard, N. L., "The Utilization of Red Mud Waste From the Aluminum Industry." Alcoa Research Laboratories, East St. Louis, Illinois, Mid American Minerals Conference, AIME, 1958.

DEFINITION OF COMPUTER TERMINOLOGY

1. Confidence Level - Probability, in per cent, that a hypothesis shall satisfy a given test. For example, if we wish to be 95 per cent confident that two mean values differ we are willing to draw an incorrect conclusion only ont time in twenty.

2. Significance - a "yes" or "no" statement on whether or not a given hypothesis should be retained or rejected. For example, if a correlation coefficient is significant at a given confidence level then we conclude that a linear relationship exists. If a correlation coefficient is insignificant, we are required to conclude that a relationship does not exist.

3. Correlation coefficient - An index of the strength of linear relationship between the changes of two variables. For example, $r_{xy} = 0.65$ means that 65 per cent of the variation between x and y is due to a linear relationship. The correlation coefficient is a way of relating the data but in no way indicates a cause-effect relationship between the variables. The question of cause and effect is an engineering problem rather than a statistical one.

4. Per cent of variation explained - The amount of variation explained be a model divided by the total variation. A least squares model that explains 25 per cent of the variation in the dependent variables will yield a $r_{xy} = .50$ or $r^2_{xy} = .25$.

5. t-test - statistic for comparing samples of data to determine whether or not the difference between their mean values are significant.

IDENTIFICATION OF LABORATORIES AND PROCEDURES

1. BCR - Bituminous Coal Research, Monroeville, Pennsylvania. BCR furnished an analytical procedure for determining total sulfur in the reacted sorbents. The procedure is unpublished and was transmitted by private communication from Mr. R. Young.

2. CT&E - Commercial Testing and Engineering Company. All analytical tests on coal, ash and sorbents were performed in the CT&E laboratory in Birmingham, Alabama under the direction of Mr. Lloyd Taylor. American Society for Testing Materials Methods C-25-67 and D-271-64 were used for sorbents, sulfur, coal and ash analyses. The C-25-67 method determines per cent sulfur trioxide in the reacted sorbent. The BCR method was used by CT&E for sulfur determinations in some cases.

3. NAPCA - National Air Pollution Control Association, Cincinnati, Ohio. An in-house sulfur test for solid sorbents was used as a check against the C-25-67 and BCR methods. Per cent SO_3 is determined using the NAPCA test.

4. TVA - Tennessee Valley Authority, Chattanooga, Tennessee. TVA used a Leco High Temperature Induction Furnace with a semi-automatic titrator for determination of total sulfur in the reacted sorbents.